Micro-level Porosimetry of Virtual Cementitious Materials
Structural Impact on Mechanical and Durability Evolution

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Micro-level Porosimetry of Virtual Cementitious Materials
Structural Impact on Mechanical and Durability Evolution

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Summary

Understanding the microstructure of cement paste is the basis of a study towards properties and behaviour of cementitious materials. It is attractive exploiting modern computer facilities for this purpose, favourably competing with time-consuming and laborious experimental approaches. This study aims at bringing material studies into virtual reality through a comprehensive computational framework that is composed of three parts as described below.

The first part deals with generating virtual representations of hardening cement composites at micro-scale, starting with producing a paste of randomly packed cement grains at the fresh state. A DEM-based dynamic packing process is used for this purpose to obtain, not only paste with high density but also that with a wide particle size range. The next stage involves simulation of the microstructure during hydration, based on an improved version of the well-known vector approach. The proposed model denoted ‘eXtended Integrated Particle Kinetics Method’ (XIPKM) includes the following improvements: a multi-component particle model to take major cement compounds and the pozzolan into account, a numerical technique to capture the complex contact between expanding particles (a crucial issue in vector approaches), and finally a concept to avoid the extreme computational effort in generating a very large amount of fine particles. Furthermore, a numerical procedure is proposed to obtain the basic penetration rates of different minerals instead of using a laborious calibration process commonly used in vector approaches.

In the second part, two computational porosimetry methods to explore the pore network characteristics are developed. The first method denoted ‘Random Node Structuring’ (RaNoS) characterises the pore space, based on analysing the configuration of a system of random points dispersed in the pore space. These random points are further employed, together with an enhanced version (for a more efficient size assessment of irregular pores) of the well-known stereological technique – star volume measure (SVM), to estimate the pore size distribution. The second porosimetry method named ‘Double-Random Multiple Tree Structuring’ (DRaMuTS) is an enhanced version of RaNoS, whereby the topology of the pore structure is further efficiently explored by a system of concurrent virtual trees growing and branching randomly in pore space, configured by a robotics-inspired path planning algorithm. Based on topological information attained by the tree systems, the pore space is then converted into a cylindrical tube network for directly estimating permeability. Based on the pore configuration obtained by the porosimetry methods, 2D representative samples to study the tensile damage response of porous materials in bulk as well as interfacial transition zone (ITZ) are proposed, whereby extremely demanding 3D FEM modelling is dismissed but the impact of the 3D pore space is nevertheless taken into account.

In the final part, several tests are carried out on cement pastes with/without blended pozzolanic admixtures, i.e. rice husk ash (RHA) by applying the presented methodologies, aiming at assessment of the impact of different design parameters
(e.g., w/c, cement fineness and RHA blending percentage) on pore characteristics, permeability and tensile damage behaviour. The relations between the pore structural features are discussed. Furthermore, the minimum size for existence of a representative volume element (RVE) for various pore characteristics as well as tensile damage response is also studied. RHA-blending is shown to improve transport-based capacities but causes a reduction in Young’s modulus, in tensile strength and ductility.
Samenvatting

Vanuit de analyse van de microstructuur van cementgebonden materialen, is het mogelijk de eigenschappen en het gedrag van het materiaal te beschrijven. Dergelijke handmatige analyses vinden gebruikelijk plaats middels experimenteel onderzoek en blijken in de praktijk zeer tijdroddend. Het ligt het voor de hand om deze taak met behulp van computeranalyses uit te voeren. Dit proefschrift is er op gericht de materiaalkundige analyse van cementgebonden materiaal virtueel uit te voeren. Aan de basis van het proefschrift staat een omvangrijk rekenkundig kader, opgebouwd uit drie hoofdonderdelen.

Het eerste onderdeel richt zich op het virtueel genereren van de microstructuur van het cementgebonden materiaal en de invloed van het hydratatieproces. Allereerst dient er een basis voor het materiaal te worden gegenereerd, inclusief een willekeurige structuur van (cement)deeltjes. Het genereren en schikken van de diverse materiaaldeeltjes is gebaseerd op een Discrete-Elementen Methode (DEM) simulatie. Niet alleen een hoge dichtheid van het virtuele materiaal, maar ook een hoge diversiteit in deeltjesgrootte wordt hierdoor bereikt. Vervolgens wordt de invloed van het hydratatieproces op de microstructuur van het materiaal gesimuleerd, waarbij een aangepaste en verbeterde variant van de zogenaamde ‘Vector Approach’ is toegepast, aangeduid als ‘eXtended Integrated Particle Kinetics Method (XIPKM).’ De volgende aanpassingen en verbeteringen zijn hierbij geïmplementeerd: het deeltjesmodel is opgebouwd uit meerdere bestanddelen, zodat zowel de werking van het aanwezige cement als het puzzolaan volledig kunnen worden beschouwd. Ten tweede is er een numerieke methode ontwikkeld voor het beschrijven van het complexe gedrag bij contact tussen uitzettende deeltjes (van cruciaal belang bij het toepassen van Vector Approaches). Daarnaast is er een concept ontwikkeld dat het mogelijk maakt een grote hoeveelheid kleine deeltjes te genereren, zonder dat daar extreme rekenkracht voor benodigd is. Tot slot maakt een numerieke methode het mogelijk de penetratiegraad van diverse mineralen te bepalen. Dit voorkomt het bewerkelijke kalibratieproces dat gebruikelijk wordt toegepast in Vector Approaches.

Het tweede onderdeel is toegespitst op de ontwikkeling van twee rekenkundige analytische technieken voor het bepalen van de karakteristieke eigenschappen van een porueus materiaal. Dit staat bekend als de zogenaamde ‘porosimetry.’ Eigenschappen zoals porievolume, -oppervlak, -diameter en absolute dichtheid zijn enkele voorbeelden van deze karakteristieken. De eerste porosimetry methode is aangeduid als ‘Random Node Structuring,’ afgekort tot RaNoS. Deze methode is gebaseerd op het analyseren van de configuratie van een systeem van willekeurige punten, die zich bevinden in de poriënruimte. In combinatie met ‘Star Volume Measure’ (SVM), een bekende stereologische techniek, kan het systeem van willekeurige punten gebruikt worden om de distributie van poriegrootte te bepalen. De tweede methode is aangeduid als ‘Double-Random Multiple Tree Structuring,’ afgekort tot DRaMuTS. In feite is deze methode een uitgebreide versie van het reeds
besproken RaNoS: de aanwezige poriënruiµte wordt onderzocht door een systeem van virtuele bomen willekeurig in deze ruimte te laten groeien en vertakken (Tree System). De configuratie en werking van dit systeem is gebaseerd op path planning algoritmes vanuit de robotica-industrie. Zodra het Tree System de poriënruiµte voldoende in kaart heeft gebracht, wordt deze ruimte omgezet in een netwerk van holle buisjes. Op deze wijze wordt direct inzicht in de permeabiliteit van het virtuele materiaal verkregen. De output van beide porosimetry methoden wordt toegepast om een representatief 2D-model van het virtuele materiaal te genereren, zonder dat de invloed van de drie-dimensionale poriënruiµte verloren gaat. Daarnaast is het toepassen van 3D FEM modellen niet aan te raden vanwege de benodigde hoge rekenkracht. De verkregen 2D-modellen staan aan de basis van het bestuderen van de invloed van trekkrachten in het poreuze materiaal: op micro niveau is de invloed op een cementdeeltje zelf, maar ook de invloed ter plaatse van de overgangszone tussen eventuele toeslagmaterialen en de cementdeeltjes (‘Interfacial Transition Zone’ - ITZ) onderzocht.

Het laatste onderdeel is gericht op het uitvoeren van een parametrische studie, op basis van het ontwikkelde virtuele cementgebonden materiaal zoals beschreven in de voorgaande onderdelen. Hierbij wordt gekeken naar diverse samenstellingen van het materiaal, bijvoorbeeld met of zonder de aanwezigheid van puzzolanen, zoals rice husk ash (RHA). Daarnaast wordt de grootte van de cementdeeltjes gevarieerd, alsmede het toevoegingspercentage RHA. De invloed van de diverse parameters op de porie-eigenschappen, permeabiliteit, treksterkte eigenschappen wordt uitvoerig beschreven. Het toevoegen van RHA blijkt een gunstige invloed te hebben op de fysische eigenschappen van het materiaal met betrekking tot (cellulair) transport. Echter blijkt er een negatieve invloed op de treksterkte, elasticiteitsmodulus en ductilititeit.

(Vertaald door F.K. Pawiroredjo MSc).
# List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>2D</td>
<td>two-dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>three-dimensional</td>
</tr>
<tr>
<td>DEM</td>
<td>discrete element method/modelling</td>
</tr>
<tr>
<td>DOH</td>
<td>degree of hydration</td>
</tr>
<tr>
<td>DOP</td>
<td>degree of percolation</td>
</tr>
<tr>
<td>DRaMuTS</td>
<td>double-random multiple tree structuring</td>
</tr>
<tr>
<td>FEM</td>
<td>finite element method</td>
</tr>
<tr>
<td>IPKM</td>
<td>integrated particle kinetics model’</td>
</tr>
<tr>
<td>ITZ</td>
<td>interfacial transition zone</td>
</tr>
<tr>
<td>MIP</td>
<td>mercury intrusion porosimetry</td>
</tr>
<tr>
<td>PC</td>
<td>Portland cement</td>
</tr>
<tr>
<td>PoG</td>
<td>porosity gradient</td>
</tr>
<tr>
<td>PoSD</td>
<td>pore size distribution</td>
</tr>
<tr>
<td>PSD</td>
<td>particle size distribution</td>
</tr>
<tr>
<td>PSR</td>
<td>particle size range</td>
</tr>
<tr>
<td>RaNoS</td>
<td>random node structuring</td>
</tr>
<tr>
<td>RHA</td>
<td>rice husk ash</td>
</tr>
<tr>
<td>RSA</td>
<td>random sequential addition</td>
</tr>
<tr>
<td>RVE</td>
<td>representative volume element</td>
</tr>
<tr>
<td>SSA</td>
<td>specific surface area</td>
</tr>
<tr>
<td>SSE</td>
<td>self-sealing effect</td>
</tr>
<tr>
<td>SVM</td>
<td>star volume measure</td>
</tr>
<tr>
<td>ThSD</td>
<td>throat size distribution</td>
</tr>
<tr>
<td>UR</td>
<td>uniform at random</td>
</tr>
<tr>
<td>w/b</td>
<td>Water to binder (mixture) ratio</td>
</tr>
<tr>
<td>w/c</td>
<td>Water to cement ratio</td>
</tr>
<tr>
<td>XIPKM</td>
<td>extended integrated particle kinetics model’</td>
</tr>
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Chapter 1 Introduction

1.1 Concrete as a particulate and porous material at different levels of its microstructure

Though used in construction industry for centuries, concrete is still one of the most popular materials for buildings and infrastructures (Figure 1.1). The long-lasting use of concrete comes from advantages as to its economy, geometrical flexibility, high fire-resistance and durability, etc. Numerous researches have been and are still being carried out to improve the performance as well as the economic aspects of the concrete material, at the same time meeting increasing environmental demands.

From the structural engineering point of view, concrete at macro-level is considered a continuous and homogeneous material, of which physical and mechanical features nonetheless originate from its underlying meso- and micro-structure. Concrete is a particulate material on the different levels of the microstructure. Beside its granular nature, a system of pores is located between the particles, thereby making concrete a porous medium at the different levels as well.

![Figure 1.1 An example of a concrete structure (AULA building, Delft University of Technology, The Netherlands)](image)
Particulate structure

The material structure of concrete can be classified from high to low into three observation levels: meso-level, micro-level and nano-level. The meso-level can be observed and associated with dimensional units ranging from mm to cm. At this level, concrete can be considered a composite material, composed of river gravel or crushed rock aggregate and sand. The aggregates are densely packed to form a stiff particle-based skeleton, stabilized by a hardened cement binder (cement matrix) (Figure 1.2a). Going to the micro-scale, the cement binder appears to be of granular nature as well. Portland cement (PC) grains of different sizes (ranging from 0.1-100 µm) in the fresh state are packed in a watery environment, filling the open places between the aggregates. In time cement grains hydrate, i.e. its major mineral compounds chemically react and solidify with the water. This is a time-evolutional process that produces increasing amounts of solid products, e.g., calcium silicate hydrates (CSH) enveloping the residual grains and calcium hydroxide (CH) crystallizing into new particles in pore space. The expanding particles interfere, thereby forming an interconnected network structure between the aggregate particles (Figure 1.2b). Details on cement hydration and cement microstructure can be

![Concrete as particle-structured materials at different scales. (a) meso-level (source by [2]); (b) micro-level (source by [4]); (c) nano-level: ‘inert product’ (left) and outer product (right) of ‘CSH gel’(source by [6]).](image-url)
obtained elsewhere [4,7]. Finally, zooming on the CSH gel as the main component of the cement paste demonstrates the particulate nature of concrete on nano-level. Figure 1.2c shows two types of CSH gel observed by transmission electron microscopy [6]. The ‘inner product’ appears to consist of globular particles, whereas the ‘outer product’ seems to have a fibrous structure.

Porous medium

A particle-based structure obviously contains openings or pore (void) space between the particles. At meso-level, the microstructure can still be considered continuous, since the spaces between aggregates are filled by cement paste. Pores appearing at this scale might be entrapped or entrained air voids located in the cement paste or at interfaces [6,8]. Entrapped air voids occur inadvertently by deficiencies during the construction process. In some cases, entrained air voids are produced intentionally by a chemical admixture to protect concrete against damage from freezing and thawing. At micro-scale, attention is given to capillary pores in the matured cement paste. These pores are indeed spaces between particulate hydration products left after the withdrawal of water by the hydration reaction. Because the capillary pores are gradually filled up by the hydration products, the capillary pore volume reduces in time to a certain value at ultimate stage of hydration. By then, the hydration process stops due to the shortage of water. At nano-level, pores exist in the CSH gel between the nano-particles and are known as gel pores.

Pore size in matured cement pastes widely ranges from a few nanometres to a few millimeters. Of the above-mentioned types of pores, the capillary pores at a micro-level exert major effects on transport processes in concrete. The air voids, ranging from about 20 µm to a few millimeters [6], are discrete and thus do not affect the permeability of concrete. Since the gel pores have sizes of a few nanometers being only one order of magnitude larger than the size of the water molecules, the movement of the water in gel pores does not contribute to the cement paste permeability, but aid the hydration process [8]. Although the capillary pores at micro-level decrease in size as well as volume during the hydration process, the pores at ultimate hydration stage may be still connected to form a percolated pore network at micro-level allowing for transport through the cement paste.

Transport-based durability aspects are studied in this thesis. Hence, the focus will be particularly on the particle-based structure composed of hydrated cement grains and particulate hydration products and on the capillary pores that are inserted between the solid particles at micro-level.

1.2 Pore characteristics and porosimetrics

One of the most important challenges in concrete engineering and research is to acquire an understanding of the pore network structure and of its influence on the physical, mechanical and durability properties of concrete. Indeed, the strength, elasticity properties and permeability are affected not only by the porosity but also by the size, shape and spatial distribution of pores. The capillary pore structure at
micro-level is extremely complex, tortuous and heterogeneous as a result of the wide size range, irregular shapes and complex hydration evolution of hydrated cement grains. At a certain degree of hydration, all pores are connected to form a percolated network. The porosity of the cement paste in a zone close to aggregates, known as the interfacial transition zone (ITZ), is higher than that in the bulk zone. Specifically, a gradient structure exists in the ITZ whereby the porosity increases from the bulk zone and reaches a maximum value at the aggregate surface. Characterization of the pore structure is therefore difficult and complicated. Several methods have been used for the characterization of the pore structure of the cement pastes. The porosimetries, the methods used to investigate the pore structure, can be categorized into ‘indirect’ and ‘direct’ methods [9].

Indirect methods are those in which pore characteristics are inferred or derived from the data of measurements based on some assumptions, for example, density, permeability to fluids, capacity of gas absorption, and so on. The (MIP), which was first introduced to concrete technology by Edel’man [10], is the most common approach to characterize capillary pores in cement pastes. The well-known Washburn equation [11] is applied to estimate the pore size distribution based on the mercury intrusion data. This evaluation invokes two assumptions: (1) pores are cylindrical and (2) they are evenly accessible from the outer surface of the specimen.

Direct methods are based on direct observations (images) of plane sections of the porous materials. The porosity, sizes and shapes of pores are obtained by mathematical analysis of the image data. The most common techniques among direct porosimetries in cement paste are successively optical microscopy (OM), scanning electron microscopy (SEM) and quantitative image analysis, where the first two ones are for generating images of material microstructures and the last involves the mathematical treatment of image data to obtain two- or even three-dimensional pore features. The OM can provide images of structures that are below the view capacity of human eyes. This method was applied by Andersen and Thaulow [12] to highlight the presence of capillary pores in concrete. SEM produces images with a much higher resolution than those obtained by OM. Lange et al. [13] carried out experiments to characterize the pore structure of cement pastes, cement pastes blended by silica fume and of mortars by using the SEM technique. Similar researches have been carried out by Willis et al. [14]. Wood’s metal was used to fill the pores enhance contrast in the BSE images.

Surveys of direct and indirect porosimetries for cementitious (cement-based) materials can be found in [9,15-16]. For a detailed description of experimental porosimetries, see [8].

1.3 Virtual cementitious materials

1.3.1 Drawback of experimental porosimetries

Experimental studies on cementitious materials involving the production of specimens, specimen pre-treatment, set up and executing tests are extremely time-
Introduction

consuming, laborious and expensive. Because the microstructure of a hydrated cement paste continuously changes over a long period of time, production of specimens at different ages would require a great deal of time. Pre-treatment of specimens, e.g., drying the specimens or slicing the specimens and polishing the surfaces (for image techniques), is also difficult and requires special equipment. Forcing mercury to intrude a specimen under the high pressure in the MIP experiment needs complex and costly tools. The SEM instrumentation and tests are also very expensive. Aligizaki [8] also states that different techniques yield different values for similar pore structure parameters. For this reason, several experimental methods are used, sometimes on the same specimen, to obtain unbiased results by combining the available information.

Experimental porosimetries have other shortcomings in addition to being time consuming, labour intensive and thus costly. The assumption that pores in hydrated cement paste are cylindrical is never fulfilled. In addition, the so-called bottle necks in the pore system [17] are neglected and the pore accessibility at the surface is rather limited. As the result, the pore sizes obtained by MIP can be orders of magnitude smaller than those obtained by image analysis. The image-based techniques though based on direct observation of the microstructure provide information that is of two-dimensional (2D) nature. Stereological and mathematical morphology methods [16] nevertheless exist to extrapolate the 2D information to the spatial presentation of pores, but structural isotropy needs to be guaranteed.

Preparation techniques of specimens and measurement techniques may change the microstructure of cement paste, too. For example, pre-treatment of the specimen, most often drying, can change the microstructure of hardened cement-paste significantly. The removal of free water in capillary pores creates capillary pressure that will cause shrinkage of the specimen, resulting in a reduced porosity as well as changes in the microstructure of the cement paste. The measurement of saturated permeability of cementitious materials is hampered by a time-dependent reduction of the flow rate because of the so-called ‘self-sealing effect’ (SSE) [18]. This phenomenon is the consequence of changes in pore structure during the process due to dissolution and precipitation of ions along the flow paths, continuing hydration by water saturation, flow path blocking by movement of loose particles under high pressure and swelling of the CSH gel due to re-saturation.

1.3.2 Computational simulation of cementitious materials

An overview of computational works on cementitious materials

The fast and continuing advances of computing facilities nowadays promote doing research on virtual materials as a more economic and reliable option. Several computer-based models have been developed in the last few decades for simulating cementitious materials and their behaviours at different levels of its microstructure.

On the meso-scale, the packing capacity of aggregates in (high performance) concrete is of engineering interest. Generally, modelling systems for such packing
can be divided into two groups: random sequential addition (RSA) and discrete element method (DEM). The RSA systems [19-21] are popular in concrete technology; however, they ignore particle interaction mechanisms, so particles are placed rather than packed as occurs in practice. Dynamic DEM systems were developed to avoid such limitations [8-14], whereby particle interaction and thus dynamic packing can be simulated. Several researches on aggregate packing [22-25] and optimum packing [22,26] in concrete using DEM systems have been carried out. DEM is also applied to develop models of the rheological behaviour of fresh concrete [27-30]. Additionally, numerous models have been developed to predict elastic moduli, mechanical behaviour and the fracture process using the finite element method (FEM) [31-37], DEM [38-40] and the lattice model [41-42].

The simulation on micro-scale of the hydration process and of the microstructural evolution has received major attention by researchers. According to Lin [43], the various models for microstructure of cement during hydration can be categorized as ‘macro-mathematical models’ [44-47] and ‘micro-numerical models’ [48-55]. The micro-numerical models were further classified by Bishnoi and Scrivener [49] into ‘vector approaches’ and ‘discretization approaches’, and into ‘single-component models’ and ‘multi-component models’. Simultaneously, several computational methods have been presented to investigate mechanical properties and fracture process of cement pastes at micro-scale [56-61].

On the nano-scale, the focus is on modelling of the nanostructure of CSH gel and on its evolution during hydration of PC. Several models [6,62-66] are proposed for description of CSH as colloid structure of jennite (CSH substance) and of the gel pores.

Modelling approaches

The ‘vector approach’ and ‘discretization approach’ are the two main methods to computationally represent geometries of materials. In the ‘discretization approach’ also called ‘digital-image-based models’, a volume of material is geometrically discretized and represented by a lattice system of simple fine elements. If all

Figure 1.3 2D sections of model samples representing hydrating cement pastes modelled by ‘discrete approach’ (left) (source by [1]) and ‘vector approach’ (right) (source by [5]).
elements are cubes, the system is referred as ‘voxel system’ (similar to pixel system in the digital image acquisition), where each voxel represents only a relevant material phase. An advantage of the voxel-based approach is the ability to model geometrically complex objects. The finer voxels are used, the more accurately the actual geometry of a material volume is modelled. This, however, increases the number of used voxels, especially in case the material is constituted of parts or particles whose sizes are small relative to the size of computational representative volume. If voxel-based approach is used to model cement paste, for examples, the number of voxels would depend on the size of the smallest model particle whereas the size of computational volume would depends on the size of the largest model particle. As the sizes of cement particles can range in around four orders of magnitude, therefore, the number of voxels used to represent the computational volume can attain trillions; this causes obviously difficulty or even impossibility for simulation because of computational limitation. To be applicable to simulating cement, only a limited range of particle sizes is modelled using this approach.

In the ‘vector approach’ the geometry of a material volume is computationally characterized by vector information about locations, directions, sizes and shape parameters of simple-shape elements (e.g., spheres, cubes and tetrahedrons). The vector approach is usually used to model granular materials such as cementitious materials, where each actual particle of an arbitrary shape is represented by a model particle of a simple shape. The number of model particles, therefore, depends on the number of actual particles as opposed to the large number of model particles that depends on the large ratio of the largest size to the smallest size of particles in the discretization approach. However, use of the elements of simple shapes in modelling that disregards the actual shapes of real particles is a disadvantage of this method. Moreover, the vector approach is also known to be computationally expensive for calculation of contacts or overlaps between model particles. Figure 1.3 illustrates the computational volumes of hydrating cement paste by the ‘discrete approach’ and ‘vector approach’.

1.3.3 Porosimetry applied to virtual cementitious materials

Porosimetry strategies applied to simulated materials have advanced as a consequence of the development of the computer-based representation of cementitious materials. The ‘medial axis algorithm’ [67] and ‘maximum ball algorithm’ [68] are the methods that can be applied to explore pore space and estimate pore size distribution (PoSD) for general virtual porous materials. The two methods are applicable to 3D voxel-based representations of materials. The pore space in these techniques is transformed into an equivalent network of local pores and throats. The sizes of pores and pore throats are determined by the erosion and partition technique. Navi and Pignat [69] employed the ‘morphological thinning and partitioning of the void space’ (MTPVS) to characterize PoSD on virtual cement pastes generated by their model [52]. The MTPVS technique consists of three stages: thinning, rebuilding, and computing equivalent radius to partition the pore space into a collection of the individual pores. In addition, Navi and Pignat used an algorithm proposed by Hosen and Kapelman [70] to calculate the degree of
connectivity of the pore space. This algorithm is based on a clustering process of voxels in which the specimen is successively sliced into layers from the upper side to the bottom side and overlap in pore phase between two adjacent layers. Bent et al. [71] and Ye et al. [72] used somewhat similar algorithms to define the pore connectivity. Moreover, Ye [73] developed an algorithm to directly evaluate PoSD by filling the pore space with testing spheres of increasing radii, starting at a certain point. Hu and Stroeven [74-75] combined stereological and mathematical morphology (i.e. opening) techniques to sections in order to derive the PoSD and the depercolation threshold of capillary pores. They additionally applied, as an alternative, a 2D version of the local porosity theory of Hilfer [76-77].

1.4 Objectives and outlines of this research work

1.4.1 Objectives of research

This study aims at developing a comprehensive methodological framework for virtual micro-scale representation of cementitious materials by a novel material model, characterization of pore structure by new porosimetry techniques that are applicable to the virtual porous materials, evaluation of the permeability of the materials by an economical pore-scale network model and investigation of the influence of pore characteristics on mechanical and transport properties of cementitious materials.

A new material model for the simulation of hydration and microstructural evolution of cementitious materials

As afore-mentioned, the micro-numerical models for simulation hydration and microstructural evolution of cement are classified into the ‘discretization approach’ and the ‘vector approach’.

The microstructure by the ‘discretization approach’ is discretized and characterized by a lattice system of voxels (3D pixels), each of which represents a relevant phase. CEMHYD3D [48,78-81] developed originally by Bentz and Garboczi at NIST (National Institute of Standards and Technology, USA) appears to be the most advanced and widely used model of this category. It can include the four major cement clinker phases as well as silica fume and inert filler. Moreover, most of the practical shapes of cement grains can be simulated. The microstructural development by hydration is simulated by the cellular-automaton (CA) algorithm [82] that governs the mutual conversion of voxel phases (e.g., pore to solid) during hydration. In spite of several advantages, CEMHYD3D still suffers from a common problem of the digital-image based system that the microstructure is limited by the voxel size. Particles and capillary pores with sizes close to or smaller than the voxel size cannot be represented. If the voxel size is reduced to adapt to small particles, the number of voxels will become excessively large. Moreover, the large particles do not need to be described with such a fine resolution, leading to difficulties and a waste of computation efforts. Furthermore, the boundaries of unhydrated parts of cement grains as well as the CSH layers covering the unhydrated parts do not remain
as practical visualization (Figure 1.4). This is due to the CA operator as indicated by Bishnoi [1].

HYMOSTRUC, developed originally by van Breugel [55,83-84] and successively upgraded by Koenders [85] and Nguyen [86], IPKM by Navi and Pignat[52], SPACE by Stroeven [87], µic by Bishnoi and Scrivener [49] and CCPM [51] are examples of models based on the ‘vector approach’. A common point of these models is the description of the microstructure by locations and set of radii of individual spherical particles that can be stored in vector type data. This makes a much smaller appeal on computer memory than the voxel-based approach. The microstructural evolution is based on the assumption that surfaces of hydrating cement grains grow inward with a rate controlled by a kinetics model. This hydration rate is also affected by reduction factors reflecting the contacts between particles during expansion and the decrease of water for chemical reactions. In HYMOSTRUC and CCPM this effect of inter-particle contact is implicitly taken into account by a statistical approach assuming that the hydration rate of a particle depends only on size, ignoring the actual interferences between individual particles. In IPKM, SPACE and µic, this contact effect is directly included by determining the free area of each particle (parts not in contact with other particles). IPKM, SPACE and µic are restricted to single phase cementitious materials (e.g., tricalcium silicate (\(\text{C}_3\text{S}\))), whereas the multi-mineral phase concept is included in HYMOSTRUC and CCPM. By HYMOSTRUC and CCPM, however, hydration mechanisms of the different mineral phases are not considered separately but are represented by an average rate that controls the homogenized spherical core representing the unhydrated mineral phases. Despite including the four main cement minerals in the model cement grains, only two hydration products of \(\text{C}_3\text{S}\), i.e., CSH and CH, are included in HYMOSTRUC and only one representative product is included in CCPM.

Another limitation of the above-mentioned models is that particles are generated by the RSA algorithm; the contact mechanisms between particles as well as between particles and rigid surfaces (of aggregates) are not realistically described as

![Figure 1.4](image_url)  
*Figure 1.4  Comparison between a SEM image (left) (source by [4]) and a slice from CEMHYD3D of hydrated cement paste (source by [1]).*
mentioned in Section 1.3.2. Furthermore, the particle generation by RSA cannot cope with high particle densities (maximum density of 0.385 for mono-sized particle packing [19]) or large numbers of fine particles in a model paste.

In this study, a novel model named XIPKM (eXtended IPKM) will be developed based on the ‘integrated particle kinetics model’ (IPKM). It can account for the four main cement minerals, i.e., tricalcium silicate (C₃S), dicalcium silicate (C₂S), tricalcium aluminate (C₃A) and tetracalcium aluminoferrite (C₄AF) as well as for a pozzolanic admixture (silicon dioxide – SiO₂). The particle and kinetics models in IPKM are extended in order to explicitly include the main minerals and their hydration products. The evolution of the particle system to a more realistic geometry and topology is guaranteed in this hydration model. The effects of temperature, hydraulic pressure and shrinkage, etc., are not considered in the scope of this study.

In this study, particle packing in the fresh state will be simulated by an advanced dynamic DEM system. The packing of a fresh paste in a container is implemented by a dynamic mixing compaction process. Particles are initially placed into a much larger container, whereupon the container volume is gradually reduced by moving its boundaries inward. In this way, not only the particle contacts are realistically simulated, but also very dense pastes can be obtained. The resulting structure is subsequently used as a starting point for the hydration simulation.

The basic hydration rates of particles in the vector-based models are commonly determined by a calibration process with trial values. Frequent iterations make this a very time-consuming procedure. In the present study, a numerical procedure will be proposed to directly determine such hydration rates based on the hydration data collected from various existing experiments.

The expansion of cement grains and the nucleation and growth of particulate hydration products during the hydration process require an adequate computing method. The changing complex interferences between the constituents make the calculation of this process difficult. This complex interaction is not given accurate attention in the literature. In XIPKM, the expansion of particles during hydration will be simulated by a specially developed numerical technique.

**Novel porosimetries applied to vector-based virtual materials**

One of the key advantages of using the virtual representation of a material is that the 3D microstructure of the material exists explicitly. The 3D pore characteristics of a virtual specimen can be obtained by analysing the pore structure directly, not by inferring experimental data or by extrapolating 2D image data.

The difficulty here is that the shape, size and location of the constituents are explicitly modelled, however, the pore system is not obtained yet. All space that remaining in the representative specimen is pores. As a consequence it is not simple to characterise the pore structure of the virtual specimen.
Most of the available algorithms to investigate virtual pore structures are voxel-based methods or image-based methods applied to 2D sections of a virtual specimen, even though the microstructure is simulated by the vector approach; this means that the pore space is discretized into a lattice system of voxels. Each of these algorithms, moreover, is specifically developed for only one pore feature (e.g., connectivity of pore); a general porosimetry able to study most of the important pore features does not exist yet.

In this thesis, two methods will be proposed that are applicable to the vector-based (particle-based) microstructure. Hence, they take less computation effort than those for voxel data and so are much faster. Various pore characteristics, *i.e.*, porosity, pore distance distribution, pore size distribution, degree of connectivity (definitions are given in Chapter 3) can now be characterised by a unique procedure by either of the two porosimetries.

As mentioned in Section 1.3.3, Navi and Pignat [88] used the voxel-based MTPVS (Morphological Thinning and Partitioning of Void Space) to analyse the pore sizes by means of two stages: erosion and dilation of pore space. Ye [73] used an algorithm whereby the pore space is filled with spheres at different steps; the size of spheres increases in steps and the total volume of spheres at each step is cumulated building a function to characterise the pore size distribution. Hu and Stroeven [74, 89] used the mathematical morphology technique ‘opening’ to characterise 3D pore size distribution on 2D sections. In this research, a stereology technique, named ‘star volume method’, is applied to measure the pore sizes directly. The volume-based pore size distribution can be derived from those measurements.

Several studies demonstrate and visualize the existence of the ITZ inserted between aggregate surfaces and bulk of cement matrix. However, a formula to determine the ITZ thickness is not given clearly yet. Moreover, the ITZ thickness varies for different structural parameters. This study proposes a mathematical procedure to define the ITZ thickness based on data of the pore gradient structure existing in an ITZ.

### A tube-network for permeability estimation

Durability properties of concrete in many cases depend on penetration possibilities of water and other harmful substances into the material by way of the percolated pore system. Hence, the transport-based durability of concrete is highly related to the permeability of cement paste (with the assumption that permeability of aggregates is much smaller than that of cement paste). The methods for predicting the permeability of a porous medium can be classified into two categories: mathematical models and numerical models.

One of the most well-known mathematical models to characterise permeability of porous media is the Kozeny-Carman formula [90-92] that is expressed by
where the permeability $k$ is related to four parameters: porosity $\phi$, specific surface area $S$ (i.e., the pore area per unit volume of the porous medium), hydraulic tortuosity $T$ and shape factor $\beta$. For a virtual porous medium these parameters can be determined from the pore structural data except the tortuosity. Matyka et al. [90-92] investigated the tortuosity of the 2D random porous medium by numerically solving flow through the medium and then expressed the tortuosity as a function of porosity. Based on morphological techniques, Hu [16] showed tortuosity to be proportional to the volume fraction of aggregates on macro-level. On the pore-scale of cement paste the tortuosity, however, is much more complex as can be seen in the Figure 1.5.

Several methods have been developed for transport problems at pore-scale through general porous media. Bentz and Martys [93] developed a finite difference method (FDM) solver to compute the permeability of 3D porous media under incompressible Stoke flow conditions. The voxels representing the pore space are utilized for FDM grids; again, the results depend on the voxel size and high computational effort is required at small voxel sizes. The effort in solving flows through porous media can be reduced by converting the pore space to a cylindrical tube-network system. The system of tube axes can be obtained by a number of techniques. Øren and Bakke [94-95] proposed an algorithm to skeletonize the pore space based on a thinning process. Silin et al. [68] developed an algorithm to construct the tube network constituted by voxel-based spherical local pore bodies connected by cylindrical pore throats. Navi and Pignat [52] used a similar scheme to Silin’s to convert pore space of simulated cement pastes. A different point is that the largest spheres are defined mathematically as inscribed spheres between four particles and the throats are those between three. Catalano et al. [96] applied the Delaunay triangulation and Voronoi diagram in 3D to construct the tube network of
discrete granular porous media. Though these are effective techniques, in general, these methods are still time-consuming due to iterative procedures (e.g., thinning process).

In this thesis, a new method will be presented to convert the vector-based pore space to a tube network structure requiring less computational effort. The tube axis network will be extracted from a tree-like structure that is used to explore the pore space in the porosimetry stage. The throat sizes of the tubes can be determined directly along the tube axes. The effect of highly irregular shapes of pores will be incorporated in this model as well. The model will be validated by comparing the permeabilities of virtual cement pastes to those computed by a finite element method Stokes solver.

**Implications of microstructure and pore characteristics on elasticity moduli and tensile damage of cement pastes**

Recent developments in nano-indentation instruments makes it nowadays possible to measure the intrinsic elastic properties of most of the constituent phases in hydrated cement pastes. Hence, the macro elastic properties can be predicted by different analytical homogenization techniques [57-58] or computational methods [59-61].

Strength of matured PC has been shown to be directly proportional to the gel-space ratio by the Powers-Brownyard model. This infers that porosity is the only property of pore space that influences the compressive strength of the cement paste. The other pore characteristics (e.g., pore size distribution) can be neglected. In contrast, those characteristics cannot be neglected when damage initiation is considered. This study aims at assessment of the impact of porosity and pore size distribution on damage initiation. Furthermore, the difference in damage evolution between the ITZ and bulk zone is studied. A comparison in damage behaviour between plain and pozzolanic-blended cement pastes is also foreseen.

**1.4.2 Outlines of research**

The content of this thesis is presented in seven chapters, in accordance with the flow chart in Figure 1.6.

Chapter 2 deals with the simulation of the evolution of microstructure of cementitious pastes during hydration. The pastes at the fresh state are described by packing of cement (pozzolanic) grains in the watery environment realized by an advanced dynamic DEM system. The particle geometry, hydration kinetics and particle evolution during hydration process are simulated by the ‘eXtended Integrated Particle Kinetics Model’ (XIPKM). This is an extension of the IPKM model (for simulation of single-component C₃S grains) to a new model that accounts for different main cement compounds (minerals) and for pozzolanic blend. This chapter also introduced new computational techniques that are used in the simulation. A numerical method is proposed to estimate the basic penetration rate of the particle reaction front based on experimental data.
Chapter 3 presents a novel porosimetry that is applicable to virtual porous materials. It is designed to be compatible with particle-based model materials, but it is also applicable to voxel-based model materials. The method, denoted ‘Random Node Structuring’ (RaNoS), investigates the pore structure based on a generated system of uniform at random dispersed nodes and a proposed algorithm for connecting such nodes. In addition, the ‘Star Volume Measure’ (SVM), a technique from stereology, is employed and modified to estimate pore size and throat size. Several characteristics of pore structure, which are difficult to obtain by experimental approaches, can be derived by these proposed methods.

Chapter 4 describes a tube network model, named ‘tube model’, for solving the slow, saturated and incompressible flow at pore scale through the virtual porous medium to estimate the permeability of the material. The tube network is constructed based on a porosimetry named ‘Double-Random Multiple Tree Structuring’ (DRaMuTS), an enhanced version of RaNoS to efficiently explore the topology of the pore structure with a system of concurrent virtual trees that grow randomly in pore space. The main trunks extracted from the virtual tree system are used as the axes of the tube network. The tube diameters are measured by the SVM. The influence of irregular-shape of pores on flow in model tubes will be taken into account. The permeabilities of cement pastes computed by the ‘tube model’ are compared to those by a FEM Stokes solver.

Chapter 5 & 6 are application parts. Effects of various parameters, e.g., cement fineness, water/binder ratio, pozzolanic blending, on pore characteristics and permeability of cementitious pastes are discussed in Chapter 5. Chapter 6 discusses the effects of pore characteristics on elasticity moduli and on tensile damage behaviour. The differences in properties and damage evolution are investigated as a result of different pore size distributions, different porosities and pore structures in ITZ and bulk zone. The effect of RHA blending is considered.

Finally, summaries, conclusions and recommendations are given in Chapter 7.
Introduction (Chapter 1)

- **Methodologies**
  - Microstructural simulation of hydrated cementitious materials (Chapter 2)
  - Computational porosimetries on virtual porous media (Chapter 3)
  - Permeability estimation on virtual porous medium (Chapter 4)

- **Applications**
  - Investigation of pore characteristics and permeability of cementitious materials (Chapter 5)
  - Implication of microstructure and pore characteristics on elastic properties and damage behaviours of cementitious materials (Chapter 6)

Conclusion (Chapter 7)

*Figure 1.6 Flow chart of the thesis.*
Chapter 2 Microstructural simulation of hydrated cementitious materials*

Since the microstructure of a hardened cementitious material continuously varies over a long period of time (i.e., couple of decades), performing experimental tests on specimens at different ages to record the microstructural developments is extremely time-consuming. Thanks to the continued improvement of computer facilities, simulating materials becomes a more economical alternative to study material behaviour, predict its properties and improve the performance of cementitious materials.

This chapter presents a novel computational model to simulate the 3D matured cement paste taking into account the influence of water to binder ratio, pozzolanic admixtures blending, fineness of particle mixture, mineral composition, particle structure and saturation conditions on the hydration process and microstructural evolution. The influences exerted by temperature, hydraulic pressure and shrinkage, etc., are considered outside the scope of this study. The whole process is initiated by simulating the packed particle structure of cement paste in the fresh state, a mixture of (pozzolanic blended) unhydrated cement grains and water. The packing simulation is implemented in the advanced dynamic discrete element simulation software, HADES. The influence of shapes of actual cement particles on the packing as well as hydration is neglected in this study: the cement grains are simulated by spherical particles. The agglomeration of cement particle during the packing simulation is also ignored. The size of the cubic representative container is based on the mean distance between aggregate grain surfaces. Accounting for the full size range of (pozzolan) cement grains (0.01–100 µm) would not be economic, since the total number of grains can reach tens of billions. Therefore, procedures are proposed to reduce the number of particles in the model by limiting the particle size range, however still guaranteeing the proper influence of the missing particle in the simulation. The hydration process and the microstructural evolution of the paste are then simulated by a new model, i.e., the ‘eXtended Integrated Particle Kinetics Model’ (XIPKM). The cement and pozzolanic grains in the fresh state are assumedly spherical and composed of the main mineral compounds. The geometric

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* Parts of this chapter were published elsewhere (Le et al. [5])
evolution of the hydrating particles is controlled by a kinetics model. New computational techniques to capture the expansion of and contact between particles during hydration are presented in this chapter. A numerical method is proposed to estimate the basic penetration rates (significant parameters of the model characterising the hydration rate) based on existing experimental data. The results obtained from four model samples of plain and pozzolanic blended cement are compared with experimental data from different authors.

In Chapter 3 a novel method to investigate the pore structure is presented and in Chapter 4 a method to measure the permeability. These methods can be applied to the (blended) matured cement paste the microstructure of which generated by the hydration model. The pastes generated by this model are also used to study the implications of microstructure and pore characteristics on elasticity modulus and tensile damage in Chapter 6.

2.1 Introduction

2.1.1 Production and composition of cement

Portland cement (PC) is produced by mixing limestone, clay and other materials heated in a kiln at around 1450° C at which partial fusion occurs and clinker nodules are formed. The clinker is then mixed with a small amount of gypsum and ground in ball mills into a fine PC powder. The details of the production process of the PC are given in Taylor [7].

The composition of cement can be described either by the oxides or by the minerals. The oxide composition of cement includes calcium oxide (CaO), silicon oxide (SiO₂), aluminium oxide (Al₂O₃), ferric oxide (Fe₂O₃) and sulphur trioxide (SO₃) as well as small amounts of other oxides. The oxides combine to form mineral compounds of the cement. PC chiefly consists of four main mineral compounds, i.e., tricalcium silicate, dicalcium silicate, tricalcium aluminate and tetracalcium aluminoferrite, gypsum and other less important minerals. Direct determination of the mineral composition (mass percentage) would be a very complex procedure. However, a simpler oxide analysis is available for determination of the oxide fractions. The mineral composition can be derived from the oxide fraction using the Bogue calculation (examples can be found in [97]). For convenience, the Bogue notation of the oxides and the main mineral compounds listed in Table 2.1 and Table 2.2 are used in this thesis.

| Table 2.1 Chemical notations in cement science |
|---------|---------|---------|---------|---------|---------|
| Formula | Notation | Formula | Notation | Formula | Notation |
| CaO     | C        | Al₂O₃   | A        | SO₃     | S        |
| SiO₂    | S        | Fe₂O₃   | F        | H₂O     | H        |
### Table 2.2 Mineral compounds of Portland cement

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase name</th>
<th>Formula</th>
<th>% weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricalcium silicate</td>
<td>Alite</td>
<td>C₃S</td>
<td>50-70%</td>
</tr>
<tr>
<td>Dicalcium silicate</td>
<td>Belite</td>
<td>C₂S</td>
<td>15-30%</td>
</tr>
<tr>
<td>Tricalcium aluminate</td>
<td>Aluminate</td>
<td>C₃A</td>
<td>5-10%</td>
</tr>
<tr>
<td>Tetracalcium aluminoferrite</td>
<td>Ferrite</td>
<td>C₄AF</td>
<td>5-15%</td>
</tr>
</tbody>
</table>

#### 2.1.2 Particle size distribution and fineness of cement

PC contains particles that vary in size from about 0.01 to 100 µm. The various particle sizes of cement are usually characterised by the particle size distribution (PSD) function. The PSD function expresses the cumulative volume fraction of particles of sizes smaller than a given size. The PSD depends on the grinding process used to produce cement. A common way to represent the PSD of cement is using the Rosin-Rammler function [85, 98]:

\[
F(s) = 1 - \exp(-bs^n)
\]

where \( s \) is the particle size and \( b \) and \( n \) are specific constants. One of the methods to determine the PSD is laser diffraction (Mastersizer 2000, Malvern Instrument Ltd., UK).

The fineness of the PC depends on the degree of the cement grinding. In general, the fineness is represented by the specific surface area (SSA), which is the total surface area of cement grains per unit of their mass. The hydration rate is promoted by a larger SSA, resulting in higher strength and lower permeability. The most common method to measure the SSA of a cement type is the Blaine air permeability test (Blaine fineness), described in ASTM C204-11. The Blaine fineness of PC usually ranges from 300-500 m²/kg. The SSA of cement can also be numerically derived from its PSD data using an equation proposed in [7]:

\[
\overline{S}_{SSA} = \frac{6 \times 10^5 \times SF}{\rho_{ce}} \sum f_i \bar{d}_i
\]

where \( \rho_{ce} \) is the cement density in kg/m³, SF is the shape factor that equals 1 for spherical particles and \( f_i \) is the volume fraction of material consisting of particles having a mean size of \( \bar{d}_i \) in unit of µm. \( f_i \) and \( \bar{d}_i \) are obtained by discretizing the PSD function.

#### 2.1.3 Water to cement ratio

A cement paste in the fresh state is a mixture of unhydrated cement grains in water. It is usually characterised by the initial mass ratio between water and cement, named water-to-cement ratio or w/c. This ratio is an important parameter for performance design of the concrete; the lower the w/c ratio is, the higher will be the strength and
durability into account. The volume fraction of cement material in the total paste $f_{ce}$ is related to the w/c ratio by the following equation (assuming the water density equal to 1 g/cm$^3$):

$$ f_{ce} = \frac{1}{1 + \frac{\rho_{ce}}{\rho_w} w_c} $$

(2.3)

where $\rho_{ce}$ is the cement density in g/cm$^3$ (around 3.150 g/cm$^3$ or 3150 kg/m$^3$), $\rho_w$ is the water density (1 g/cm$^3$) and $w_c$ is the w/c ratio.

### 2.1.4 Cement hydration

The hydration of PC is a process of chemical exothermic reactions between the cement minerals and water that produces an increasing amount of solid containing different products called ‘hydrates’. The hydrates act as glue making different particles (including aggregates in concrete) adhere to each other to form a binder that hardens in time. The hydration process is influenced by many factors such as composition, cement fineness, w/c ratio, temperature, moisture conditions, etc. Hydration results in a complex time-evolutional microstructure of cement paste. Different mineral compounds experience different hydration stages with different hydration rates, heat evolution and mechanisms. The complex hydration of PC can be described by the following basic reactions given in [48,82]:

\[
\begin{align*}
C_3S + 5.3H & \rightarrow C_{17}SH_4 + 1.3CH \\
C_2S + 4.3H & \rightarrow C_{17}SH_4 + 0.3CH \\
C_3A + 6H & \rightarrow C_3AH_6 \\
C_3A + 3C\bar{S}H_2 + 26H & \rightarrow C_6A\bar{S}_3H_{32} \\
2C_3A + C_6A\bar{S}_3H_{32} + 4H & \rightarrow 3C_4A\bar{S}H_{12} \\
C_4AF + 3C\bar{S}H_2 + 30H & \rightarrow C_6A\bar{S}_3H_{32} + CH + FH_3 \\
2C_4AF + C_6A\bar{S}_3H_{32} + 12H & \rightarrow 3C_4A\bar{S}H_{12} + 2CH + 2FH_3 \\
C_4AF + 10H & \rightarrow C_3AH_6 + CH + FH_3
\end{align*}
\]

where the names of the hydration products are listed in Table 2.3. For a detailed description of the hydration process of the minerals at different stages, see [7,83]. The process of hydration can be characterised by the degree of hydration (DOH) $\alpha(t)$ that is defined by

$$ \alpha(t) = \frac{V_{ce}^r(t)}{V_{ce}^0} = 1 - \frac{V_{ce}(t)}{V_{ce}^0} $$

(2.12)

where $V_{ce}^0$, $V_{ce}^r$ and $V_{ce}$ are the initial cement volume, the reacted cement volume and the current cement volume, respectively.
Table 2.3 Principal phases of cement paste during hydration process [82]

<table>
<thead>
<tr>
<th>Compound name</th>
<th>Formula</th>
<th>Density (g/cm$^3$)</th>
<th>Molar volume (cm$^3$/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricalcium silicate</td>
<td>$C_3S$</td>
<td>3.21</td>
<td>71.0</td>
</tr>
<tr>
<td>Dicalcium silicate</td>
<td>$C_2S$</td>
<td>3.28</td>
<td>52.0</td>
</tr>
<tr>
<td>Tricalcium aluminate</td>
<td>$C_3A$</td>
<td>3.03</td>
<td>89.1</td>
</tr>
<tr>
<td>Tetracalcium aluminoferite</td>
<td>$C_4AF$</td>
<td>3.73</td>
<td>128.0</td>
</tr>
<tr>
<td>Gypsum</td>
<td>$C\bar{S}H_2$</td>
<td>2.32</td>
<td>74.2</td>
</tr>
<tr>
<td>Calcium silicate hydrate</td>
<td>$C_{1,7}SH_4$</td>
<td>2.12</td>
<td>108.0</td>
</tr>
<tr>
<td>Calcium hydroxide</td>
<td>CH</td>
<td>2.24</td>
<td>33.1</td>
</tr>
<tr>
<td>Ettringite</td>
<td>$C_6A\bar{S}<em>3H</em>{32}$</td>
<td>1.7</td>
<td>735.0</td>
</tr>
<tr>
<td>Monosulfoaluminate</td>
<td>$C_4A\bar{S}H_{12}$</td>
<td>1.99</td>
<td>313.0</td>
</tr>
<tr>
<td>Hydrogarnet</td>
<td>$C_3AH_6$</td>
<td>2.52</td>
<td>150.0</td>
</tr>
<tr>
<td>Iron hydroxide</td>
<td>$FH_3$</td>
<td>3.0</td>
<td>69.8</td>
</tr>
<tr>
<td>Water</td>
<td>H</td>
<td>1.0</td>
<td>18.0</td>
</tr>
</tbody>
</table>

Globally speaking, a hardening cement paste consists of (1) unreacted cement, (2) hydration products and (3) capillary pores containing the remaining free water. The total solid volume of unreacted cement and hydration products increases during the hydration process, leading to a reduction in volume of capillary pores. Apart from the free water located in the capillary pores, there is also an amount of water in the gel pores of the calcium silicate hydrate (CSH gel). The loss of the remaining water due to evaporation can lead to shrinkage in the cement paste, which is usually referred to as ‘drying shrinkage’. Another kind of shrinkage is the so-called ‘chemical shrinkage’, caused by the reduction in volume of the water due to conversion into the chemical bound water. This implies the volume of the hydration products to be smaller than the total volume of the cement and the water from which it originates. Figure 2.1 is an illustration of the volumetric microstructural evolution of cement paste during the hydration process.

![Microstructural evolution of cement paste during hydration](image)
Chapter 2

2.1.5 Pozzolanic admixtures

Portland cement (PC) production contributes by about 6% to global emissions of CO$_2$. Reduction of the PC content in the binder exerts therefore a direct positive effect on such emissions. Partial replacement of the Portland cement by pozzolanic mineral admixtures has been proven a liable option. Moreover, blending cement paste with pozzolanic admixtures can generally increase the strength and durability of the cement paste as well as of the concrete [86,99-100]. In recent years, therefore, pozzolanic admixtures have been used widely in producing high performance concretes. The hydration of pozzolanic admixture can be briefly presented by the following formula [82]:

$$S + 1.1CH + 2.8H \rightarrow C_{1.1}SH_{3.9}.$$ \hspace{1cm} (2.13)

Pozzolanic silica-rich admixtures, such as fly ash, silica fume and rice husk ash may improve the cement paste as well as of the concrete by physical and chemical mechanisms. Specifically,

(1) the small particle sizes activate the micro-filler effect, \textit{i.e.}, the pozzolanic particles fill the spaces between the coarser cement particles as well as the spaces between cement particles and the aggregates surface, leading to improved particle packing density;

(2) the chemical reaction between the silica minerals and the calcium hydroxide produced during hydration of the PC forms an increasing solid volume of the CSH gel, thus resulting in an additional reduction in capillary porosity.

These physical and chemical effects therefore significantly improve the strength and transport-based durability of the cement paste as well as of concrete.

When a cement paste is blended by a pozzolanic admixture, the paste is characterised by the water-to-binder ratio ($w/b$) that is the mass ratio of water to the total amount of the binder, \textit{i.e.}, the mixture of cement and pozzolanic admixture. The volume fractions of cement $f_{ce}$ and of pozzolanic admixture $f_{poz}$ to the total volume of the paste are respectively given by:

$$f_{ce} = \frac{1}{1 + \frac{1}{\rho_{ce} w_b} + \frac{p_{bl} \rho_{ce}}{1 - p_{bl} \rho_{poz}}}$$ \hspace{1cm} (2.14)

$$f_{bl} = \frac{1}{1 + \frac{1}{p_{bl} \rho_{poz} w_b} + \frac{1 - p_{bl} \rho_{poz}}{p_{bl} \rho_{ce}}}$$ \hspace{1cm} (2.15)

where $\rho_{ce}$ and $\rho_{poz}$ are cement density and pozzolan density, respectively, $p_{bl}$ is the blending dosage (percentage by mass of replacement) equal to the mass ratio of the pozzolanic admixture to the binder, and $w_{b}$ is the $w/b$ ratio.
2.2 Packing simulation of fresh (blended) cement paste

To simulate the microstructure of the (blended) cement paste during hydration, the paste in the fresh state that consists of cement grains packed in the watery environment is required to be modelled. In this research, the model specimen representing the cement paste, which is produced in a cubic region (container), contains discrete spherical particles representing the cement grains in the fresh state. By the assumption on spherical cement particles, the shape effect of actual cement particles on the packing as well as hydration of the paste is considered outside of this study’s scope. The simulation of the packed structure of the particles in a realistic way is required to capture the grain-packing process in casting concrete. The simulation of cement paste in the fresh state therefore consists of two consecutive steps: generation of model particles in a container and packing simulation of such particles.

2.2.1 Generation of particles

For the generation of model particles, the total number and individual sizes of the particles are required that correspond to a given volume of particles, a particle size range (PSR) and a particle size distribution (PSD). The total volume of particles depends on the volume (size) of the representative cube and the volume fraction of the particles (Eqs. (2.14)-(2.15)). Firstly, therefore, the size of a specimen needs to be determined. Section 2.2.1.1 discusses how the size of the representative cube is chosen. The full PSR of the constituent material also requires some modification to be in conformity with the model specimen size, which is presented in Section 2.2.1.2. Finally, determination of the number of generated particles and the size of each particle is presented in Section 2.2.1.3. A proposed concept to reduce the total number of particles for an efficient simulation is discussed in 2.2.1.4.

2.2.1.1 Model specimen size

Since the simulation of cement paste aims at reproducing a region between aggregate grains, the side length of the representative specimen should be chosen equal to the mean surface spacing of neighbouring aggregates. Diamond et al. [101] estimated this distance to vary in range of 75-100 µm in ordinary concrete. Hu et al. [102], who investigated the influence of the volume fraction and of the aggregate size range on particle spacing, revealed that this distance ranges between 40-130 µm for an aggregate composed of 1-30 mm grains. The side length of the specimen in this research is therefore chosen in the range of 75-130 µm.

2.2.1.2 Reduced particle size range

In this research, the ratio of the maximum particle size of model cement to the linear container’s size is limited to 0.4, which means the container’s size is larger than 2.5 times the maximum particles size. This limitation is to assure the representative nature of the specimen (see Section 5.1 for more details). When the side length of a specimen is 100 µm and the real cement has a particle size range of 0.1-100 µm, for example, a maximum size 40 µm of the model particles will be selected. As a result
of this restriction in maximum size of model particles, the fineness of the model particles exceeds that of the real cement.

Since the fineness of particle paste is one of the most significant parameters influencing the overall hydration rate, the size range needs to be additionally modified to make the fineness of model paste equal to that of the real cement. Hence, the lower bound of the original PSR is adjusted to a value larger than the minimum size of the real cement particles, so that the overall fineness of the model particles will match that of the real cement. Consequently, the original PSD is modified in accordance with the narrowed size range as shown in Figure 2.2. The modified PSD function is derived from the original PSD by

$$F'(d) = \frac{F(d) - F(d_{\text{min}})}{F(d_{\text{max}}) - F(d_{\text{min}})}$$

(2.16)

where \([d_{\text{min}}, d_{\text{max}}]\) is the size range of the model particles and \(F\) and \(F'\) are the original and modified PSD functions, respectively. It is noticed that different values of minimum particle size will result in different fineness values of the model paste. To determine \(d_{\text{min}}\), an iterative procedure is used, whereby trial values of \(d_{\text{min}}\) will be selected into Eq. (2.2) until the desired fineness is obtained.

2.2.1.3 Number and sizes of model particles

To derive the sizes and the associated numbers of particles, the PSR in this research is discretized in a set of size steps. For instance, the cement size range of 1~30 µm is discretized into a 300 equidistant sampling sizes of [1.0, 1.1, ..., 29.9, 30.0]. For each sampling size, the corresponding particle volume fraction is derived from the given PSD and thus the number of particles corresponding to this sampling size can be calculated. The calculated number of particles at each sampling size is obviously not an integer and thus needs to be rounded down. The rounded value will leave a residual volume of particle which is ignored. The cumulative residual volume over all sampling sizes would result in a significant difference of the generated particle volume from the desired particle one. To solve this problem, the generation process
starts from the larger to the smaller sampling sizes, at each of which the residual volume from rounding is cumulated to the volume for generating particles in the next smaller size. The process of particle generation is defined by the following equation

\[
n_i = \text{floor} \left( \frac{f_{\text{psd}}(d_i) \Delta s V_{\text{par}}} {\pi d_i^3 / 6} + V_{\text{residue}}^{i-1} \right), \quad d_i = d_{\text{max}} - \Delta s(i - 1)
\]  

(2.17)

where \( n_i \) is the number of generated particles at size \( d_i \). \( f_{\text{psd}}(d_i) \) gives the value at size \( d_i \) of the density PSD function that is the derivative of the cumulative PSD function (Eq. (2.1)), \( \Delta s \) is the size interval, \( V_{\text{par}} \) is the total volume of cement or pozzolanic particles of the model sample, ‘floor’ denotes the rounding down function, and \( V_{\text{residue}}^{i-1} \) is the residual volume of particles from rounding in the previous step \( i-1 \). The total number of particles is therefore obtained by

\[
n_{\text{tot}} = \sum_{i=1}^{N} n_i.
\]  

(2.18)

where \( N \) is the total number of sampling size \( d_i \).

### 2.2.1.4 Reduction of particle number

Although the particle size range is narrowed as afore-mentioned, it is still computationally demanding to simulate a paste because of the excessive number of grains. Indeed, the number of model particles can reach into millions to even billions in case of simulating cement paste of high fineness or low w/b ratio, or when dealing with a cement paste blended by fine-grained admixtures. Although only taking a small volume fraction of the total particles (i.e., 1-5%), the very fine particles can take up a very large fraction of the total number of particles (i.e., larger than 90%). Therefore, it would be computationally beneficial if this small fraction is neglected in the packing simulation. There are a couple of arguments supporting this. Such fine particles have little influence on the packing structure of larger particles because of their small sizes and low volume fraction. Moreover, they only affect the hydration rate at initial time and will be soon merged into the deposits of the hydrating larger particles and therefore have little influence on the microstructural evolution of the matured paste.

The size under which the particles are neglected in the packing simulation is referred to as the ‘threshold size’ (Figure 2.3). The impact of such neglected particles on the microstructure during hydration of the paste will be discussed in Section 2.3.2.
2.2.2 Packing simulation by dynamic DEM

As mentioned in the previous chapter, a high density of random particle paste (e.g., larger than 0.6) cannot be achieved by random sequential addition (RSA). Another simulation technique to obtain a dense random packing of particles can be referred as ‘mechanical contraction’ by Williams and Philipse [103], based on an algorithm to remove overlap in a system of particles initially configured using standard Monte Carlo techniques. Although the volume fraction can reach to 0.6~0.7 by this technique, it is only applicable for spheres and spherocylinders. Moreover, this cannot account for arbitrary particle shapes as well as mechanical contacts between particles during a dynamic packing process.

The packing of the fresh (blended) cement particles in this study is simulated by HADES (HAbanera’s Discrete Element Simulator) [26,104-106]. HADES is an advanced concurrent algorithm-based dynamic DEM system that allows mechanical interactions between particles of arbitrary shapes as well as between the particles and the rigid container surfaces. Furthermore, several inter-particle forces such as spring forces, cohesion forces, damping forces and friction forces can be employed. HADES renders possible implementing particle packing in containers with periodic boundaries, rigid boundaries or mixed periodic-rigid conditions.

A Newtonian system is used during the packing simulation to have particles translating and rotating inside the container space. Inter-particle contact simulated by very small overlap between particles leads to the building up of forces that thereupon cause both particles involved to react accordingly. The type of reaction forces can be manipulated to yield different effects for structure formation such as either in the case of aggregate or of cement particles. In contrast, static DEMs shift particles locally for elimination of the overlap. Dynamic DEM will offer more realistic simulation conditions for concrete compacted by vibration. For a detailed description of HADES, see [26].
Two types of model containers are used to represent cement pastes under different conditions, *i.e.*, 

1. The cubic container bounded by six periodic boundaries represents the infinite paste or the ‘bulk zone’.
2. The cubic container bounded by two rigid walls at two opposite sides and by four periodic boundaries at the other sides represents the space between the aggregate surfaces.

The packing of particles in the container is implemented by a dynamic process; the particles are initially dispersed in a large container using a random sequential positioning process and are then compacted by gradually reducing the container size (by moving all sides inwards) until the desired \( \text{w/b} \) ratio is achieved. It is noticed that tendency of cement particle agglomeration that can be partly prevented by use of superplasticizers is neglected during packing simulation. Figure 2.4 illustrates a dynamic packing process used to simulate cement paste between two nearby aggregate surfaces. In this way, not only the particle contacts are realistically simulated but also very high density can be attained in the paste. This can never be achieved by the random sequential addition algorithm.

### 2.3 Hydration simulation of (blended) cement paste

The microstructural evolution of (pozzolanic blended) cement paste during hydration in this study is modelled by the ‘\text{eXtended Integrated Particle Kinetics Model}’ abbreviated as XIPKM. XIPKM is an extension of the ‘\text{Integrated Particle Kinetics Model}’ (IPKM) developed by Navi and Pignat [52,69,107] to simulate the evolution of a \( \text{C}_3\text{S} \) microstructure during hydration based on the vector approach. In IPKM an anhydrous core of \( \text{C}_3\text{S} \) grain is modelled by individual sphere, the surface of which is considered to be the ‘reaction front’ that grows concentrically inwards.
The evolution of the reaction front during hydration is controlled by the different mechanisms modelled by mathematical or kinetic models; in other words the hydration kinetics are integrated into the particle model. IPKM simulates the hydration of every individual particle, using kinetic laws that depend on the particle size, the remaining water and inter-particle contacts with neighbouring particles. The produced CSH during hydration is modelled as growing concentric layers enveloping the particle by which it is generated. The produced CH that nucleates and grows in the pore space is modelled as individual particles. In this study, the particle model and the hydration kinetics of the IPKM are ‘extended’ for taking into account the major cement compounds and the pozzolan. It is assumed that the cement grains consist of four main minerals, i.e., tricalcium silicate (C\textsubscript{3}S), dicalcium silicate (C\textsubscript{2}S), tricalcium aluminate (C\textsubscript{3}A) and tetracalcium aluminoferrite (C\textsubscript{4}AF), whereas the pozzolanic grains are composed of only silica (SiO\textsubscript{2}) and an inert phase.

2.3.1 Formation of eXtended Integrated Particle Kinetics Model

2.3.1.1 Chemical reactions

Hydration of hydraulic materials involves a chemical reaction with water. The volume change of each phase (cement components, pozzolan, free water and hydration products) can be computed via the chemical equilibrium of cement reactions given by Eqs. (2.4)-(2.11) and the compound molar volumes given by Table 2.3. In the present model, the cement particles are assumed to be composed of only four major cement compounds, i.e., C\textsubscript{3}S, C\textsubscript{2}S, C\textsubscript{3}A and C\textsubscript{4}AF. Hence, the chemical equilibrium reaction of the four mineral compounds can be expressed in relative volume ratios of water and hydration products to reactants, neglecting the gypsum reaction:

\[ 1.0V_{C3S} + 1.34V_H \rightarrow 1.521V_{CSH} + 0.610V_{CH} \]  (2.19)

\[ 1.0V_{C2S} + 1.49V_H \rightarrow 2.077V_{CSH} + 0.191V_{CH} \]  (2.20)

\[ 1.0V_{C3A} + 1.21V_H \rightarrow 1.69V_{CAH} \]  (2.21)

\[ 1.0V_{C4AF} + 1.41V_H \rightarrow 1.17V_{CAH} + 0.259V_{CH} + 0.545V_{FH} \]  (2.22)

with CSH, CH, CAH and FH being abbreviations of calcium silicate hydrate, calcium hydroxide, hydrogarnet and iron hydroxide, respectively. Similarly, the chemical equilibrium reaction of the silica (SiO\textsubscript{2}) in the form of relative volume ratios is expressed:

\[ 1.0V_S + 1.35V_{CH} + 1.87V_H \rightarrow 3.77V_{CSH} \]  (2.23)

As mentioned in Section 2.1.1, the PC clinker is usually ground with a minor amount of gypsum. C\textsubscript{3}A and C\textsubscript{4}AF react with gypsum to form ettringite (Eqs. (2.7) & (2.9)), crystalizing in the needle shape at the surface of the cement grains. When the gypsum has been consumed, the ettringite starts decomposing and thereupon reacts with additional C\textsubscript{3}A and C\textsubscript{4}AF to form the monosulphate phase (Eqs. (2.8) & (2.10)). Since the needle-shaped ettringite is formed only during the first hours of
hydration and the amount of gypsum is small, the gypsum and the ettringite formation are ignored in this model.

2.3.1.2 New particle model

In XIPKM, the cement and pozzolan grains are modelled by the so-called ‘multi-component and multi-layer spherical particle model’. Each particle in its unhydrated fresh state is assumed to be a multi-component spherical particle, partaken by the constituent components representing the four main mineral compounds and formed by spherical sectors, as illustrated at the top of Figure 2.5. The bottom of Figure 2.5 shows the model that describes the state of a hydrated particle. During hydration the unhydrated (multi-component) core of each particle gradually reacts with water, thereby decreasing in size, while the CSH amount produced by hydration of the core precipitates on the outer surface of the core itself as a shell. The shell of the CSH product is composed of two distinct layers, the ‘inner CSH’ (CSH_{in}) that substitutes the volume of the hydrated compounds and thus grows inwards and the ‘outer CSH’ (CSH_{out}) that precipitates spherically on the outer surface of the particle and thus grows outwards. The assumption that the diffusing CSH concentrates and locates at the dissolution source due to low mobility of silicate ionic species is in accordance with Bentz [78]. The surfaces of the spherical sectors (unhydrated components) are assumed to be the places where the free water (diffusing through the CSH shell) reacts with the mineral compounds. These component surfaces, referred to as the ‘reaction fronts’, grow inwards and maintain their spherical sector shape. The different penetration rates of the reaction fronts that are characterised by a hydration...
kinetics model (presented in the next section), make the radii of the components differ. When the outer CSH layer of the particle interferes with those of neighbouring particles, the outer CSH no longer precipitates at the overlap area, but evenly re-distributes onto the remaining free outer surface of the particle. A model particle is configured by geometrical data (i.e., \( r_o, r_{in}, r_{out} \) and coordinates) and fractions \( f^\lambda \) of the components, where \( \lambda \) denotes the different components representing the mineral compounds (Figure 2.5). \( r_{inert} \) of the spherical sector characterizing the inert phase of the pozzolanic particles is assumed unchanged during hydration and thus will be neglected in further considerations.

CH, CAH and FH diffuse and either nucleate randomly into crystals in pore space or precipitate on surfaces of already existing crystals \([48,78,107]\). These nucleated crystals are modelled by simple spherical particles, illustrated at the bottom (three particles on the right hand side) of Figure 2.5. The decision to nucleate a CH particle is based on the number of expected grains at time \( t \). In [52] Navi and Pignat propose the following rule:

\[
    n_{CH}(t) = n_{CH,max} \left( 1 - e^{-at} \right)
\]

(2.24)

where \( n_{CH,max} \) is the maximum number of CH grains at complete hydration and \( a \) is a constant. The two constants can be calculated following Jennings and Parrott's work \([108]\) reporting that there is one CH grain for 12.5 grains of C\(_3\)S after one day of hydration and five grains of C\(_3\)S at complete hydration. The size of a CH particle either increases during the hydration process due to the precipitation of the CH produced by the cement reaction, or decreases as a result of the pozzolanic reaction of CH.

The number of researches on diffusion and nucleation of CAH and FH is scarce; however Bentz \([48,78]\) shows that the probability of nucleation of diffusing CAH and FH is governed by an equation with a form similar to Eq. (2.24). Therefore, the nucleation of these species can be described by the following general equation

\[
    n_\lambda = n_{\lambda,max} \left( 1 - e^{-a_\lambda t} \right) \quad \lambda = CH, CAH, FH .
\]

(2.25)

It is noted that with higher mobility of calcium and aluminate ions, CH and CAH are distributed somewhat uniformly, whereas with lower mobility of ferrite ions, FH crystallizes near to a dissolution source \([78]\). CH and CAH that are produced by hydration of a particle are therefore assumed uniformly at random distributed in pore space in the present model, whereas FH is assumed distributed nearby the particle from which it is produced.

2.3.1.3 Hydration kinetic model

Three different mechanisms were introduced in the IPKM model by Navi and Pignat \([52]\) for controlling the kinetics of the reaction front of a C\(_3\)S particle, \( i.e., \) ‘nucleation and growth’, ‘phase-boundary’ and ‘diffusion’. The first mechanism is neglected, since it only controls the initial reaction until a relative small degree of
The penetration rate of the reaction front of a C<sub>3</sub>S particle <i>i</i> for the other two mechanisms can be given by a single formula:

\[
\frac{dr_{in}^i(t)}{dt} = K_o \left( \delta_{tr} / \delta^i(t) \right)^\beta C_s^i(t) C_w(t)
\]

where \( r_{in}^i(t) \) is the radius of the fresh (unhydrated) core at time \( t \), \( K_o (\mu m/h) \) is the basic rate constant and \( \delta^i \) is the thickness of the product shell that is equal to \( r_{out} - r_{in} \), where \( r_{out} \) is the outer radius of the hydration product. \( \delta_{tr} \) is the transition thickness equal to \( \delta^i \) at the time that the controlling mechanism changes from the ‘phase-boundary’ stage (\( \beta = 0 \) and \( \delta_{tr} / \delta^i \geq 1 \)) to the ‘diffusion’ stage (\( \beta = 1 \) and \( \delta_{tr} / \delta^i < 1 \)). \( C_s^i \) is a reduction coefficient related to the decrease in free surface (parts in contact with the water or pore) and calculated as the area ratio between the free surface and the total surface (assuming no contact) of the particle. \( C_w \) is a global reduction coefficient given by Rohling and cited by van Breugel \[55\] related to the decrease in water content and calculated by

\[
C_w(t) = 1 - \frac{\nu \alpha(t)}{\rho w_o + \alpha(t)}
\]

where \( \nu \) is a constant defined as the volume ratio of the total hydration products (i.e., CSH and CH) and the hydrated amount of C<sub>3</sub>S, \( \alpha \) is the degree of hydration defined as the volume ratio of the hydrated amount and the initial amount of C<sub>3</sub>S, \( \rho(g/cm^3) \) is the specific mass of the fresh material and \( w_o \) is the initial water-to-binder ratio.

The hydration rate in XIPKM is established separately for the reaction front of each mineral component by the following formula

\[
\frac{dr_{in}^{\lambda,i}(t)}{dt} = K_o^\lambda \left( \frac{\delta_{tr}^i}{\delta^{\lambda,i}(t)} \right)^\gamma C_s^i(t) C_w(t)
\]

\[
\lambda = C_3S, C_2S, C_3A, C_4AF, SiO_2
\]

in which the meaning of the symbols is the same as in Eq. (2.26), except that \( \lambda \) is attached to denote the respective components and \( \gamma \) is added to have one more parameter to control the hydration rate. \( \delta^{\lambda,i} \) is the thickness of the hydration product layer covering component \( \lambda \) that equals \( r_{out}^i - r_{in}^{\lambda,i} \) (Figure 2.5). As different components are included, the volume ratio between the total hydration product to the total hydrated amount (\( \nu \) in Eq. (2.27)) is no longer a constant and thus Eq. (2.27) for \( C_w \) is not valid in this case. \( w_o \) in Eq. (2.27) equals \( V_{w,0} / (\rho V_{m,0}) \) and \( \nu \) and \( \alpha \) can be defined as \( V_{prod} / V_{m,react} \) and \( V_{m,react} / V_{m,0} \), respectively. \( V_{w,0} \), \( V_{m,0} \), \( V_{m,react} \) and \( V_{prod} \) represent the initial water volume, the initial binder volume, the hydrated binder volume, and the total hydration product volume, respectively. This renders possible rewriting \( C_w \) in the more general form

\[
C_w(t) = 1 - \frac{V_{prod}(t)}{V_{w,0} + V_{m,react}(t)} = \frac{V_{po}(t)}{V_{w,0} + V_{m,react}(t)}
\]
where $V_{po}$ denotes the total volume of capillary pores. It is noticed that the volume of capillary pores differs from that of the remaining water; the volume ratio of water to pores reduces in time since the total volume of hydration products is smaller than that of the reacted minerals and the water from which the hydration products were obtained (Eqs. (2.19)-(2.23)). Assuming that the water-contact ratio of the pore surface equals the reducing water-to-pore volume ratio, $C_w$ is further modified as follows

$$C_w(t) = \frac{V_{po}(t)}{V_{w,0} + V_{m,react} (t)} \cdot \frac{V_w(t)}{V_{w,0} + V_{m,react} (t)}$$

(2.30)

where $V_w(t)$ is the remaining water volume located in the capillary pores. In case of full water saturation, the pore space is fully filled by water and $C_w$ is thus determined by Eq. (2.29).

When the time of hydration is discretized in a number of time steps and the hydration rate is assumed to be constant during each step, the penetration depth of the reaction front of component $\lambda$ of particle $i$ during time step $j$ can be estimated by

$$\Delta r_{m,j}^{\lambda,i} = K_0^{\lambda} \left( \frac{\delta \lambda}{\delta \lambda,j} \right)^{\beta} C_{s,j} \cdot C_{w,j} \cdot \Delta t_j$$

$\lambda = C_3S, C_2S, C_3A, C_4AF, SiO_2$. (2.31)

The hydration simulation during a time step is in many vector approach models ([49], [52] and [54]) an order-based process in which hydration proceeds successively from particle to particle. The hydration rate of a particle is proportional to the remaining water volume and the free surface ratio and, as a result, depends on water consumption and volume expansion by hydration of previous particles. So, the hydration rate of a particle depends on the order of the particles. When the system is out of water for the hydration of a particle, for example, the hydration no longer proceeds to pending particles. To avoid this order-based process in the present study, hence to simulate hydration concurrently, the coefficients in Eq. (2.31) are estimated at the beginning of step $j$ for all particles in the presented model. The amount of water available for each particle's hydration is pre-defined as well; the total remaining water volume is divided into parts by the number of particles to determine the amount of water available for hydration to a single particle. It is assumed that the proportion between these subdivided water volumes equals that between water consumption rates of the particles. Hence, the water amount available for hydration of a particle can be estimated by

$$V_{w,j}^{i} = \sum_{\lambda} K_{w,j}^{\lambda,i} V_{w,j}^{\lambda}$$

$\lambda = C_3S, C_2S, C_3A, C_4AF$ (cement)

$\lambda = SiO_2$ (pozzolan)

(2.32)

where $V_{w,j}^{i}$ is the total volume of water available at the beginning of time step $j$. $K_{w,j}^{\lambda,i}$ represents the water consumption rate of a component that is obtained by
multiplying the surface area, the penetration depth and the relative water ratio (in the chemical equations) of the particular component, divided by the time increment. Hence,

\[
K_{w,j}^{i,\lambda} = \frac{4\pi}{3} \left[ \left( r_{m,j}^{i,\lambda} \right)^3 - \left( r_{m,j}^{i,\lambda} - \Delta r_{m,j}^{i,\lambda} \right)^3 \right] f_0^i v_w^i \\
\lambda = C_3 S, C_2 S, C_3 A, C_4 A F, SiO_2
\]

(2.33)

where \( f_0^i \) is the volume fraction as well as the surface fraction (of the spherical sector) of component \( \lambda \) at the initial state, \( \Delta r_{m,j}^{i,\lambda} \) is the penetration depth calculated by the right-hand side of Eqs. (2.31) and \( v_w^i \) is the relative volume ratio of water in the reaction equation of component \( \lambda \) (Eqs. (2.19)-(2.23)). It is noted that the hydration of the components of a particle also need to be simulated simultaneously. Therefore, the amount of water available for a particle is subdivided into sub-parts, the number of which equals the number of components and each of which is only available for hydration of a single component. Hence, the water required for hydration of a component of a particle during a single time step cannot exceed the sub-part available for this component. This is expressed by

\[
\frac{4\pi}{3} \left[ \left( r_{m,j}^{i,\lambda} \right)^3 - \left( r_{m,j}^{i,\lambda} - \Delta r_{m,j}^{i,\lambda} \right)^3 \right] f_0^i v_w^i \leq \sum_{\lambda} K_{w,j}^{i,\lambda} v_w^i
\]

(2.34)

\( \lambda = C_3 S, C_2 S, C_3 A, C_4 A F \) (cement)
\( \lambda = SiO_2 \) (pozzolan)

which yields a constraint for the penetration depth:

\[
\Delta r_{m,j}^{i,\lambda} \leq r_{m,j}^{i,\lambda} - \left( r_{m,j}^{i,\lambda} \right)^3 - \frac{3 V_{w,j}^{i,\lambda} K_{w,j}^{i,\lambda}}{4\pi f_0^i v_w^i} \sum_{\lambda} K_{w,j}^{i,\lambda} \right)^{1/3}
\]

(2.35)

\( \lambda = C_3 S, C_2 S, C_3 A, C_4 A F \) (cement)
\( \lambda = SiO_2 \) (pozzolan)

Since CH is also a reactant in the pozzolanic reaction, the available CH volume also constrains the penetration depth. Hence,

\[
\Delta r_{m,j}^{i,\lambda} \leq r_{m,j}^{i,\lambda} - \left( r_{m,j}^{i,\lambda} \right)^3 - \frac{3 V_{CH,j}^{i,\lambda} K_{CH,j}^{i,\lambda}}{4\pi f_0^i v_{CH}^i} \right)^{1/3}
\]

(2.36)

where \( v_{SiO_2}^{i,\lambda} \) is the relative volume ratio of CH in the reaction equation of SiO_2 (Eq. (2.23)) and \( V_{CH,j}^{i,\lambda} \) is the CH volume available for the pozzolanic reaction of particle \( i \) that can be estimated by
\[ V_{CH,j} = \sum_i K_{CH,j}^{i,\lambda} V_{CH,j} \quad \lambda = \text{SiO}_2 \] (2.37)

where \( V_{CH,j} \) is the total CH volume at the beginning of time step \( j \) and \( K_{CH,j}^{i,\lambda} \) is the CH consumption rate of a component of the particle that can be estimated by

\[ K_{CH,j}^{i,\lambda} = 4\pi \left( r_{\text{out},j}^{i,\lambda} \right)^2 f_o^e \Delta r_{\text{in},j}^{\lambda,i} \frac{V_{CH,j}^{\lambda,i}}{\Delta t_j} \quad \lambda = \text{SiO}_2 . \] (2.38)

Besides, the penetration depth \( \Delta r_{\text{in},j}^{\lambda,i} \) cannot exceed the current radius \( r_{\text{in},j}^{\lambda,i} \). In summary, the penetration depth of the reaction front of component \( \lambda \) of particle \( i \) during time step \( j \) is given by

\[ \Delta r_{\text{in},j}^{\lambda,i} = \min \left\{ \Delta r_{\text{in},j}^{\lambda,i}, \Delta r_{\text{in},j}^{\lambda,i}, \Delta r_{\text{in},j}^{\lambda,i}, r_{\text{in},j}^{\lambda,i} \right\} \]

\[ \lambda = C_2S, C_2A, C_A, C_A \text{AF} \quad (\text{cement}) \]

\[ \lambda = \text{SiO}_2 \quad (\text{pozzolan}) \] (2.39)

where \( \Delta r_{\text{in},j}^{\lambda,i}, \Delta r_{\text{in},j}^{\lambda,i}, \Delta r_{\text{in},j}^{\lambda,i,\text{w}} \) are estimated by the right-hand sides of Eqs. (2.31), (2.35) and (2.36), respectively. In case of full water saturation, the constraint \( \Delta r_{\text{in},j}^{\lambda,i} \) is relaxed.

### 2.3.1.4 Calculation of volume change

The volume changes of the different constituents caused by the hydration of particle \( i \) during time step \( j \) can be calculated by

\[ \Delta V_{\kappa,j}^{i} = \frac{4\pi}{3} \sum_\lambda \left[ \left( r_{\text{in},j}^{\lambda,i} \right)^3 - \left( r_{\text{in},j}^{\lambda,i} - \Delta r_{\text{in},j}^{\lambda,i} \right)^3 \right] f_0^e \nu_{\kappa}^{\lambda} \]

\[ \lambda = C_2S, C_2A, C_A, C_A \text{AF} \quad (\text{cement}) \]

\[ \lambda = \text{SiO}_2 \quad (\text{pozzolan}) \]

\[ \kappa = \text{water, CSH, CAH, FH, CH}_{\text{prod}}, \text{CH}_{\text{react}} \] (2.40)

where \( \nu_{\kappa}^{\lambda} \) is the relative volume ratio corresponding to phase \( \kappa \) by hydration of component \( \lambda \), derived from the chemical equations (Eqs. (2.19)-(2.23)). Since part of the CSH volume (\( \text{CSH}_{\text{in}} \)) substitutes the total volume of the components that has reacted in this step, the CSH volume (\( \text{CSH}_{\text{out}} \)) precipitating on the surface of the particle is given by

\[ \Delta V_{\text{CSH,out},j}^{i} = \frac{4\pi}{3} \sum_\lambda \left[ \left( r_{\text{in},j}^{\lambda,i} \right)^3 - \left( r_{\text{in},j}^{\lambda,i} - \Delta r_{\text{in},j}^{\lambda,i} \right)^3 \right] f_0^e \nu_{\text{CSH}}^{\lambda} \left( \nu_{\text{CSH}}^{\lambda} - 1 \right) \]

\[ \lambda = C_2S, C_2A, C_A, C_A \text{AF} \quad (\text{cement}) \]

\[ \lambda = \text{SiO}_2 \quad (\text{pozzolan}) \] (2.41)
2.3.2 Equivalent mono-sized fine particles

As mentioned in Section 2.2.1.4, the finest particles smaller than the ‘threshold size’ are neglected in packing simulation of the cement paste in the fresh state. The impact of these particles on the microstructural evolution during hydration still needs to be taken into account. Modelling those fine particles are modelled with discrete objects would require an extreme amount of particles and thus computational effort. To overcome that problem, it is assumed that the fine particles are replaced by a number of ‘equivalent mono-sized particles’, the hydration evolutions of which are exactly the same. This assumption yields the computational benefit that only one model particle is needed to characterise the hydration evolution of all equivalent particles.

The initial diameter of the equivalent particles is determined so that their total surface area in the fresh state equals that of original finest particles. For instance, the diameter of the equivalent particles for cement $d_{oc,ce}^e$ is derived from

$$\pi \left( d_{oc,ce}^e \right)^2 n_{eq} = S_{ce,o}^f$$

(2.42)

where $n_{eq}$ is the number of equivalent particles and $S_{ce,o}^f$ is the total surface area of the original finest particles in the fresh state. Replacing $n_{eq}$ by the total volume of the fresh finest particles $V_{ce,o}^f$ divided by the volume of a single equivalent particle $\pi \left( d_{oc,ce}^e \right)^3 / 6$ with transposition of some terms, Eq. (2.42) becomes

$$d_{ce,o}^e = \frac{6V_{ce,o}^f}{S_{ce,o}^f}.$$

(2.43)

In a similar way the initial diameter of the equivalent particles representing the finest pozzolanic particles is expressed by

$$d_{poz,o}^e = \frac{6V_{poz,o}^f}{S_{poz,o}^f}.$$

(2.44)

The equivalent particles are also modelled by the particle models in XIPKM (Figure 2.5), integrated with the hydration kinetics model. Due to the small size and the low density in pore space, the equivalent particles are assumed to hydrate independently from neighbouring particles during hydration. The reduction coefficient $C_i^t$ related to inter-particle contact is thus removed from the hydration kinetics equations. The hydrating equivalent particles are implicitly included in the model specimen; they are assumed not to appear as discrete model particles but occur under the deposits of their hydration products on the generated particles (ones larger than the threshold size). This assumption is in accordance with the observation that the equivalent particles are very fast completely hydrated and they are then merged into (swallowed by) the generated particles.
To take the influence of the equivalent fine particles to the hydration of the generated particles into account, the coefficient $C_{s,j}$ in Eq. (2.31) accounting for inter-particle contacts is adjusted as follows,

$$C_{s,j} = \frac{A_{\text{free},j}^i V_j^{po} - V_j^{eq}}{A_{\text{tot},j}^i V_j^{po}}$$

(2.45)

where $A_{\text{free},j}^i$ is the area of the surface part that does not contact with other particles and $A_{\text{tot},j}^i$ is the total surface area of particle $i$, $V_j^{eq}$ is the total volume of unhydrated parts of the equivalent particles and $V_j^{po}$ is the total volume of pores between the generated particles at time $j$.

2.3.3 Algorithmic aspects

2.3.3.1 Estimation of free surface

In the present model, the effect of the free surface on the hydration rates of the reaction fronts is explicitly taken into account by the area ratio of the free surface and the total surface, $C_s^i$, determined for individual particles. To estimate the free surface ratio $C_s^i$, the ‘sampling point method’ [54] is used. A number of sampling points are evenly dispersed on the total surface of a particle. Then, the free surface ratio is numerically estimated as follows

$$C_s^i = \frac{n}{n_{\text{tot}}}$$

(2.46)

where $n_{\text{tot}}$ is the total number of the sampling points and $n$ is the number of the points inside other particles. The ‘general spiral points’ method, which has been demonstrated to be one of the most effective and simplest ways for dispersing points evenly on a spherical surface [109-110], is used in this model. The coordinates of point $k$ of $N$ spiral points on a unit sphere’s surface is given by

$$x_k = \sqrt{1 - z_k^2} \cos(\phi_k)$$

$$y_k = \sqrt{1 - z_k^2} \sin(\phi_k)$$

$$z_k = -1 + \frac{k}{N} - 1, \quad 1 \leq k \leq N$$

$$\phi_k = \left(\phi_{k-1} + \frac{3.6}{\sqrt{N}} \frac{1}{\sqrt{1 - z_k^2}} \mod 2\pi\right), \quad 2 \leq k \leq N-1, \phi_1 = \phi_N = 0$$

(2.47)

2.3.3.2 Estimation of particle expansion

The increment of the outer radius $\Delta r_{\text{out}}^i$ of particle $i$ resulting from a new product volume that has precipitated on the particle's surface governs the expansion of the particle. The relationship between the precipitating volume $\Delta V_{\text{prec}}^i$ and the corresponding radius increment $\Delta r_{\text{out}}^i$ is given by
Microstructural simulation of hydrated cementitious materials

\[ \Delta V_{\text{prec}}^i = \frac{4\pi}{3} \left( r_{\text{out}}^i + \Delta r_{\text{out}}^i \right)^3 - \left( r_{\text{out}}^i \right)^3 \right) C_v^i \left( \Delta r_{\text{out}}^i \right) \]  

(2.48)

where \( C_v^i \) is the ratio between the free volume (the part that has no contact with other particles) and the total volume of a spherical shell with a thickness equal to \( \Delta r_{\text{out}}^i \) (Figure 2.6). Eq. (2.48) is an implicit equation and cannot be solved directly for the unknown \( \Delta r_{\text{out}}^i \). If \( C_v \) can be estimated from a value of \( \Delta r_{\text{out}}^i \), nonetheless, the solution of Eq. (2.48) can be obtained by a standard numerical method for solving a nonlinear equation. Estimation of \( C_v^i \left( \Delta r_{\text{out}}^i \right) \) could be impossible by analytical means due to complex interferences of the spherical shell with the surrounding particles. Therefore, the ‘sampling point method’ is used again:

\[ C_v^i \left( \Delta r_{\text{out}}^i \right) = 1 - n / n_{\text{tot}} \]  

(2.49)

where \( n_{\text{tot}} \) is the total number of sampling points uniformly at random dispersed in the spherical shell with thickness \( \Delta r_{\text{out}}^i \), and \( n \) is the number of the points situated inside another particle as illustrated in Figure 2.6. Herein, the coordinates of a sampling point \( k \) are given by

\[ x_k = \sqrt{1 - (2u - 1)^2 \cos(2\pi v) \left( \left( r_{\text{out}}^i \right)^3 + w \left( \left( r_{\text{out}}^i + \Delta r_{\text{out}}^i \right)^3 - \left( r_{\text{out}}^i \right)^3 \right) \right)^{1/3}} \]

\[ y_k = \sqrt{1 - (2u - 1)^2 \sin(2\pi v) \left( \left( r_{\text{out}}^i \right)^3 + w \left( \left( r_{\text{out}}^i + \Delta r_{\text{out}}^i \right)^3 - \left( r_{\text{out}}^i \right)^3 \right) \right)^{1/3}} \]

\[ z_k = \left( 2u - 1 \right) \left( \left( r_{\text{out}}^i \right)^3 + w \left( \left( r_{\text{out}}^i + \Delta r_{\text{out}}^i \right)^3 - \left( r_{\text{out}}^i \right)^3 \right) \right)^{1/3} \]  

(2.50)

where \( u, v \) and \( w \in (0,1) \) are the random variables.

\[ \text{uniform at random} \]

\[ \text{sampling points} \]

\[ \text{surrounding particles} \]

\[ \text{spherical shell with thickness } \Delta r_{\text{out}}^i \]

\[ r_{\text{out}}^i \]

\[ \text{free points} \]

\[ \text{points in other particles} \]

\[ Figure \ 2.6 \quad \text{Sampling point method for estimation of the free volume ratio of a spherical grain.} \]
2.3.3.3 3D microstructure by the voxel system

The microstructure simulated by the hydration model is represented and visualized by the ‘digital-image-based’ technique or the voxel system. Herein, the microstructure of the hydrating paste is composed of the unhydrated cement, the unhydrated pozzolan, CSH\textsubscript{in}, CSH\textsubscript{out}, CH, CAH, FH and the pore space. To simplify the visualization, the constituent phases of the unhydrated core of each particle are merged into a single average phase, represented by a spherical core of which the volume equals the total volume of the individual phases. Figure 2.7 is an illustration of a microstructure visualized by the voxel system, whereby the red and yellow represent the unhydrated cement and unhydrated pozzolan, respectively. Some voxels can change phases during the cement hydration process; unhydrated cement or unhydrated pozzolan voxels can change into CSH\textsubscript{in} ones, pore voxels can change into CSH\textsubscript{out}, CH, CAH or FH ones, and CH voxels can change into pore ones (pozzolanic hydration). It is noted that this voxel system is only used for representing the microstructure of the hydrating paste and thus does not affect the hydration simulation process or calculation speed.

An advantage of this voxel system is its ability to precisely identify the phases that are located at the overlap of the growing particles (of different phases) during the hydration evolution, which is very difficult in the vector approaches. Indeed, with a vector approach, only the boundaries between phases are accurately represented, not the phases itself. Phase representation at the layer-by-layer overlap among neighbouring expanding particles cannot be uniquely represented, as illustrated in Figure 2.8a. On the contrary, with the recording-phase voxel system, the phases at the complex overlap zone can be simply characterized as in Figure 2.8b. Additionally, the voxel data are also useful for the analysis of the microstructural characteristics as well as for the transformation to a finite element method mesh for evaluation of mechanical properties.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure27.png}
\caption{Visualization of the hydrating paste with the phase voxel system. Each unhydrated multi-phase core is represented by a sphere of which the volume equals the total volume of the phases.}
\end{figure}
2.3.4 Numerical estimation of the basic penetration rate of hydration front

Model coefficient $K_\lambda^\lambda$ (Eq. (2.28)) reflects the penetration rate of the hydration front of component $\lambda$ without considering any of the reduction coefficients. A numerical calculation is proposed in this study to obtain the basic rate constants, based on the hydration data derived from physical experiments of a number of real cement pastes collected in literature. The different obtained values of $K_0^\lambda$ corresponding to the different real pastes will be analysed to form functions used to determine $K_0^\lambda$ parameters of model pastes by XIPKM.

2.3.4.1 Formulation

Consider a model cement paste representing a real cement paste of which the degree of hydration (DOH) has been experimentally obtained as a function of time. Under the assumption that, at early hydration, the penetration rate of each component is the same for all particles, the relationship between the degree of hydration (DOH) $\alpha^\lambda$ and the penetration depth $\xi^\lambda$ of component $\lambda$ is given by the following equation [111]

$$\alpha^\lambda = 1 - \sum_{i=1}^{n} f_i \left(1 - \frac{\xi^\lambda}{r_o^i}\right)^3$$  \hspace{1cm} (2.51)

where $n$ is the number of particles, $r_o^i$ is the initial radius of particle $i$ and $f_i$ is the weight fraction corresponding to the initial size $d_i$ ($d_i = 2r_o^i$). $\xi^\lambda$ can be obtained by solving the following equation that is obtained after re-arranging Eq. (2.51)

$$\left(\sum_{i=1}^{n} f_i \left(\frac{r_o^i}{r_o^i}\right)^3\right)\left(\xi^\lambda\right)^3 = \left(\sum_{i=1}^{n} f_i \left(\frac{r_o^i}{r_o^i}\right)^2\right)\left(\xi^\lambda\right)^2 + 3 \left(\sum_{i=1}^{n} f_i \frac{r_o^i}{r_o^i}\right)\xi^\lambda - \alpha^\lambda = 0.$$  \hspace{1cm} (2.52)

When the DOH of a compound $\alpha^\lambda_{\text{ref}}$, at a reference time $t_{\text{ref}}$ is known, taking the integral of $dn^\lambda_w(t)$ in Eq. (2.28) (neglecting the mechanism change at early time) from $t = 0$ to $t = t_{\text{ref}}$ yields the following equation

$$\xi^\lambda_{\text{ref}} = \int_{0}^{t_{\text{ref}}} K_0^\lambda C_s(t)C_w(t)dt$$  \hspace{1cm} (2.53)

Figure 2.8 Phase representation at layer-by-layer overlaps of two neighbouring particles during the expansion due to hydration of the particles.
where $C^\lambda_s$ is calculated by solving Eq. (2.52) with $\alpha^\lambda = \alpha^\lambda_{ref}$. $\alpha^\lambda_{ref}$ and $t_{ref}$ can be taken from the experimental hydration curve of compound $\lambda$. The penetration rate of each component is assumed to be the same for all particles, so a unique global coefficient $C_s$, accounting for the free surface reduction should be included instead of individual values $C^\lambda_i$. This overall coefficient can be obtained from the area ratio of the total free surfaces and the total spherical surface of all particles:

$$C^\lambda_s = \frac{\sum_{i=1}^{n} \left(t_{in}^{\lambda,i}\right)^2 C^\lambda_i(t)}{\sum_{i=1}^{n} \left(t_{in}^{\lambda,i}\right)^2}.$$  
(2.54)

When $t_{ref}$ is discretized into a number of even steps, Eq. (2.53) transforms into

$$\frac{\varepsilon^\lambda_{ref}}{\varepsilon^\lambda_{ref}} = \sum_{j} K_o \cdot C_{w,j} \cdot C^\lambda_{s,j} \Delta t$$  
(2.55)

where $j$ denotes the step index and $C_{w,j}$ can be calculated by Eq. (2.29) at the corresponding DOH $\alpha^\lambda_j$ at time $t_j$ (from the experimental hydration curve of $\lambda$). To obtain $C^\lambda_{s,j}$, hydration simulation of the model paste is implemented with the same penetration rate for all components. $C^\lambda_{s,j}$ is calculated by Eq. (2.54) at the time the DOH of the model paste equals $\sum \alpha^\lambda_j f^\lambda_o$ (the overall DOH at time $j$). With transposition of some terms, Eq. (2.55) becomes

$$K_o^\lambda = \frac{N \frac{\varepsilon^\lambda_{ref}}{\varepsilon^\lambda_{ref}}}{t_{ref} \sum_j C_{w,j} C^\lambda_{s,j}}.$$  
(2.56)

where $N$ is the number of time steps ($t_{ref} = N \Delta t$).

2.3.4.2 Implementation

A series of experimental hydration data of real cement pastes are used to calculate the corresponding $K_o$-values of the mineral compounds. The input data for estimating $K_o$ of the components are given in Table 2.4, whereby $f_o$ is the initial volume proportion of the components. $\alpha_{ref}$ and $t_{ref}$ denote the reference values of the DOH and the corresponding time.

$K_o$-values for C3S are plotted as a function of component proportion in Figure 2.9. The functions for $K_o$ of C3S can be estimated through linear regression analysis by means of

$$K_o^{C3S} (f_o^{C3S}) = 0.0369 + 0.041 \times (1 - f_o^{C3S})$$

where $f_o^{C3S}$ denotes the proportion of C3S (Eq. (2.33)). The $K_o$-values for C2S, C3A and C4AF are only computed as single values of 0.0064, 0.0373 and 0.0056, respectively, because of insufficient data to form functions of these components.
Hereafter, these function and values can be applied to calculate basic penetration rates for the model cement paste that represents a real cement paste with compound compositions as the inputs.

### 2.4 Verifications

XIPKM is verified by simulating the hydrated microstructures of the four physical plain and RHA-blended PC samples that have been investigated by different researchers [86,114-115]; the hydration data obtained from the simulation will be compared to those from the experimental data. The input data of the model containers representing the real samples are detailed in Table 2.5, where the $K_o$-values of the mineral components are determined by the procedure presented in Section 2.3.4.
Table 2.5 Input data for simulating microstructural evolution during hydration

<table>
<thead>
<tr>
<th>Sample names</th>
<th>W40Pc</th>
<th>W25Pc</th>
<th>W40Po10</th>
<th>W40Po20</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/b</td>
<td>0.4</td>
<td>0.25</td>
<td>0.4</td>
<td>0.4</td>
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<tr>
<td>Cement fineness (cm²/g)</td>
<td>3200</td>
<td>3120</td>
<td>4500</td>
<td>4500</td>
</tr>
<tr>
<td>RHA fineness (cm²/g)*</td>
<td>-</td>
<td>-</td>
<td>5218</td>
<td>5218</td>
</tr>
<tr>
<td>% blended RHA</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>f₀-C₃S·C₂S</td>
<td>0.542:0.278</td>
<td>0.649:0.193</td>
<td>0.714:0.101</td>
<td>0.714:0.101</td>
</tr>
<tr>
<td>:C₃A:CaAF</td>
<td>0.064:0.117</td>
<td>0.081:0.078</td>
<td>0.097:0.088</td>
<td>0.097:0.088</td>
</tr>
<tr>
<td>b, n - cement</td>
<td>0.026, 1.102</td>
<td>0.025, 1.104</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>Particle size range (µm)</td>
<td>0.35-33</td>
<td>0.37-33</td>
<td>0.26-33</td>
<td>0.26-33</td>
</tr>
<tr>
<td>RHA size range (µm)</td>
<td>-</td>
<td>-</td>
<td>0.68-33</td>
<td>0.68-33</td>
</tr>
<tr>
<td>n.o. modelled cement particles</td>
<td>17418</td>
<td>21642</td>
<td>32622</td>
<td>28384</td>
</tr>
<tr>
<td>n.o. modelled RHA particles</td>
<td>-</td>
<td>-</td>
<td>7429</td>
<td>14538</td>
</tr>
<tr>
<td>fₑₑₑₑₑₑ ***</td>
<td>0.025</td>
<td>0.024</td>
<td>0.052</td>
<td>0.052</td>
</tr>
<tr>
<td>dₑₑₑₑₑₑ,e₀ *** (µm)</td>
<td>0.63</td>
<td>0.64</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>fₑₑₑₑₑₑ,RHA,₀ ***</td>
<td>-</td>
<td>-</td>
<td>0.029</td>
<td>0.029</td>
</tr>
<tr>
<td>dₑₑₑₑₑₑ,RHA,₀ *** (µm)</td>
<td>-</td>
<td>-</td>
<td>0.83</td>
<td>0.83</td>
</tr>
<tr>
<td>K₀-C₃S·C₂S;</td>
<td>0.0557; 0.0064; 0.0513; 0.0064; 0.0506; 0.0064; 0.0528; 0.0064;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₃A:CaAF (µm/h)</td>
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<td>0.0373; 0.0056</td>
<td>0.0373; 0.0056</td>
<td>0.0373; 0.0056</td>
</tr>
<tr>
<td>K₀-RHA (µm/h)</td>
<td>-</td>
<td>-</td>
<td>0.007</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Model container size: 100x100x100 (µm); Threshold particle size: 1 (µm).

* RHA fineness computed by Eq. (2.2).
** PSD functions of cement and RHA are experimentally measured and plotted in [86].
*** f₀ and d₀ respectively denote the volume fraction (threshold fraction) and diameter of replacing ‘mono-sized particles’ (Section 2.3.2).

Figure 2.10 depicts 2D sections of the hydrated samples revealing their simulated microstructures. The sections at the top demonstrate that at the same time of hydration (90 days), the DOH of the sample with w/c = 0.4 exceeds that of the sample with w/c = 0.25, so that the unhydrated cement fraction (colour coded in red) is more significantly reduced. Furthermore, porosity of the sample (i.e., the pore fraction that is colour coded in black) with w/c = 0.25 is much lower than that of the sample with w/c = 0.4. The sections at the bottom of Figure 2.10 show that the CH fraction of the sample (colour coded in green) is reduced at higher blending dosage as a result of the higher amount of available SiO₂.

Comparisons of the degree of hydration of plain PC samples shown in Figure 2.11 indicate good agreement between the experimental results and the simulations. Note that trial values are used for the model parameters, i.e., δᵢᵣ and γ (Eq. (2.31)), until the simulation curves fit well to experimental data as in Figure 2.11. Although a calibration process is still required, the calibration for K₀-values as the most significant model parameter can be eliminated as a result of the proposed estimation of K₀-values. The total porosities of the RHA-blended PC samples obtained by
simulation and from experimental results of Nguyen [86] are compared in Figure 2.12a, while a comparison in the CH content is shown in Figure 2.12b. There are several reasons why the simulated values are different from the experimental data. For instance, the experimental data result from an indirect method (Thermo-gravimetric Analysis used to determine the CH content [86,116]), which leads to experimental biases. Moreover, the simulation is carried out with the assumption that the pastes are ideally cured condition; there is no loss of water by evaporation that occurs in reality. Figure 2.13 depicts porosity evolution of ideally cured specimens, compared to that of specimens at fully water-saturated condition. In the latter case, the pores of the specimens are assumedly fully filled with water during the hydration process. At \( w/c = 0.4 \), the fully saturated specimen does not differ much from the ideally cured specimen in porosity evolution, since the water volume at such a water/cement ratio is sufficient for hydration to proceed properly. On the contrary for specimens with \( w/c = 0.25 \), the shortage of water constrains the hydration rate of the ideally cured specimen. The full supplement of water in case of full water saturation makes the hydration of the specimen process faster, leading to a significant difference in porosity.

Figure 2.10  2D sections of the samples.
Figure 2.11  Hydration curves of plain cement samples.

Figure 2.12  (a) Porosity curves of RHA-blended PC samples and (b) CH fraction curves RHA-blended PC samples.
2.5 Conclusions and discussion

This chapter presents a multi-component integrated particle kinetic model (XIPKM) for simulating the evolution of microstructure during hydration of cement and pozzolanic admixtures. The unhydrated core of a model particle consists of four main mineral components, \( \text{i.e., } C_3S, C_2S, C_3A \) and \( C_4AF \) for cement or two components for the pozzolanic admixture, \( \text{i.e., } \text{SiO}_2 \) and inert material. The microstructure of a model paste is visualized by a digital-based ‘voxel system’.

The fine grains in a cementitious paste appear in enormous numbers, but do not have significant influence on the particle structure in the fresh state as well as in the matured state. In this study the particles of sizes below a selected threshold size are excluded from the granular packing simulation of the representative specimen. They are replaced by a number of equivalent mono-sized particles. The evolution of the mono-sized particles during hydration is similar. These equivalent particles are not included in modelling the microstructure as explicit individual model particles but as deposit layers on the existing model particles. This concept keeps the simulation computationally efficient but still yields the realistic parameters (e.g., including very fine particles in simulation).

By forming the constituent components of the unhydrated part of a particle by different spherical sectors, the hydration rate of a particle is controlled by the different penetration rates of the phases. As a result, the presented model is able to account for the changes in the constituent proportions of a particle during hydration. Contrary, in many multi-component hydration models, the constituent proportions are assumed unchanged during hydration, while the unhydrated core is described by a homogenized single phase sphere \([51,86]\). This assumption also means that the hydration rate is the same for all components, which is unrealistic since in practice different components hydrate at different rates.
Although based on the multi-component concept, CCBM [51] assumes that the hydration products are represented by a homogenized hydration product that adheres to the cement particles. Further, the extended version of HYMOSTRUC3D [86] assumes the hydration product to include only CSH and CH. In the proposed model, four distinct hydration products of the four major cement compounds are involved, i.e., CSH, CH, CAH and FH. CSH precipitates on the cement particles, CH and CAH diffuses and crystallizes randomly in the pore space and FH diffuses and crystallizes near the dissolution source. This is in agreement with the assumptions by Bentz [48] based on the mobility of diffusing ions.

By subdividing the remaining contents of water and CH (for pozzolanic reaction) according to the number of particles and then according to the number of components, the simulated hydration process can proceed concurrently, thereby avoiding an order-based procedure that is popular in vector-based approaches. This concurrent process makes the hydration simulation of the individual particles as well as the formation of the hydrate structure more realistic than the use of an order-based process.

In the hydration simulation systems based on the vector approach, the estimation of outward growth of the hydrating particles plays a crucial role in the simulation of microstructural evolution. Indeed, since the particles expand by the precipitation of the hydration products and thus gradually occupy part of the pore space, the precision in estimating the particle expansion obviously affects the reliability of measures for geometry and topology (pore continuity!) of pore space. Estimating the size increment of a spherical particle caused by a new volume of precipitated hydration products is a complicated task due to the growing complexity of interferences among particles. In the presented model, the particle expansion is estimated by a numerical procedure that accounts for such implicit interferences.

In many vector approach models, the basic rate constant of a phase is commonly determined through a calibration process [51,55,86] in which many trial values of the basic rate constants are attempted until the hydration curves (DOH vs. time curves) fit well with experimental results. Instead of a laborious calibration process, herein, a numerical procedure is proposed to obtain the basic penetration rates of different minerals from the hydration data of the experiments.
Chapter 3 Computational porosimetry for virtual porous materials

Experimental methods to investigate the pore characteristics of porous media are laborious, expensive and time-consuming. Indeed, the production and pre-treatment of specimens, test instrumentation and labour make the physical investigation of pore features a complex and costly process. Thanks to fast development of computer facilities, investigating the pore characteristics of computer-modelled porous media nowadays becomes an economic and reliable alternative.

In this chapter a novel computational method – porosimetry – is presented that explores the characteristics of the pore structures at micro-level of 3D virtual representations of porous media. The computational method is specifically efficient for vector-based (e.g., particle-based) microstructures of porous media. The method is, however, not limited to the vector-based pore structure; it can also be utilized for investigating the voxel-based pore structure. The method denoted ‘Random Node Structuring’ (RaNoS) characterises the pore space by using a system of points that are uniformly at random dispersed in the pore space. The characteristics of the pore space are investigated by analysing the configuration of such random points using various techniques.

The stereological technique ‘Star Volume Measure’ (SVM) is enhanced to measure the sizes of local 2D pore sections (or pore throats) and is extended into a 3D version to measure local 3D pore size.

These porosimetry techniques are developed to examine the pore characteristics of a general virtual porous medium and therefore they are completely applicable to the capillary pore structure of the virtual cementitious pastes generated by XIPKM (Chapter 2).

In the next chapter (Chapter 4), the RaNoS will be enhanced to be better applicable to characterise hydraulic flow through porous media and denoted as ‘Double-Random Multiple Tree Structuring’ (DRaMuTS).

* Parts of this chapter were published elsewhere (Stroeven et al. [117])
3.1 Pore characteristics

In this study the pore structure of a porous medium is characterised by the following parameters:

- Porosity
- Degree of connectivity
- Pore size distribution
- Specific surface area

The following characteristics are supplemented for the pore structure of cementitious paste at the zone between aggregate surfaces.

- Pore gradient structure
- Interfacial transition zone thickness

The characterization of the porous materials by these parameters are limited to porous materials that are composed of only two phases, i.e., solid and pore space, and the pore sizes should be in the same scale. For example, the hydrated cement paste at micro-level is assumed to consist of the solid phase and the capillary pores; the ‘gel pores’ in the CSH gel are not taken into account. Therefore CSH gel is assumed to be solid in the evaluation of the pore structure.

3.1.1 Porosity

The ‘overall porosity’ $\phi$ is the fraction of the total bulk volume that is occupied by the pore space and is expressed by

$$\phi = \frac{V_{po}}{V_{tot}} \times 100$$

(3.1)

where $V_{po}$ is the pore volume and $V_{tot}$ is the total bulk volume of the material.

3.1.2 Degree of connectivity

The overall porosity can be classified as ‘percolated pores’ and ‘isolated pores’. The percolated pores form an interconnected network of pores going through the material. When the pore structure is simulated in a representative cubic specimen, the percolated pores are defined as a network that connects to both opposite outer surfaces of the specimen. The isolated pores consist of closed pores and pores that are interconnected but are not connected to both opposite outer surfaces. The volume ratio of the percolated pores to the total pores is defined as the ‘degree of percolation’, $\alpha_{per}$, formulated by

$$\alpha_{per} = \frac{V_{per}}{V_{po}}$$

(3.2)

where $V_{per}^{po}$ denotes the total volume of percolated pores.
3.1.3 Specific surface area

A common parameter of the pore structure is the total interfacial surface area between pore space and the solid, or in simpler terms, the total pore surface area. This factor influences directly the fluid transportation through porous media. Obviously, the transportation properties are also influenced by the porosity. At the same porosity, however, the porous medium with higher pore surface area leads to a smaller permeability than the one with lower pore surface area. As a consequence, the pore surface area is usually characterised by the specific surface area $\bar{S}_{po}$ given by

$$\bar{S}_{po} = \frac{S_{po}}{V_{po}}$$

where $S_{po}$ is the total pore area.

3.1.4 Pore size distribution

The variation in pore sizes of the pore structure is commonly characterised by the pore size distribution (PoSD). In this study, the PoSD is expressed by the volume-based density (frequency) function:

$$P_{PoSD}(s) = \frac{1}{V_{po}} \frac{dV_{po}(s)}{ds} = \frac{F(s + ds) - F(s)}{ds} \quad (1/[l])$$

(3.4)

$$\int_{0}^{\infty} P_{PoSD}(s)ds = 1$$

(3.5)

where $F(s)$ expresses the fraction of the cumulative volume of pores that have sizes smaller than $s$ on the total volume of pores in the specimen. An example of PoSD function is presented in Figure 3.1.

![Figure 3.1](image-url)  
*Figure 3.1* An example of pore size distribution corresponding to a matured cement paste.
3.1.5 Porosity gradient and interfacial transition zone

The porosity of a zone close to aggregates in cement pastes, known as the interfacial transition zone (ITZ), is higher than that of the bulk zone \[54,118-119\]. Specifically, a gradient structure exists in the ITZ whereby the porosity increases from the bulk zone and reaches a maximum value at the aggregate surface. In this study, the porosity gradient (PoG) is characterised by the sectional porosity as a function of distance to the aggregate surface. When a cubic specimen with two opposite rigid walls is used to represent the cementitious paste between the aggregate surfaces, the sectional porosity is defined by the area fraction of pores on the cross-section of specimen that is parallel to the rigid walls at the considered distance. Hence, in this case, the PoG function \(P_{\text{PoG}}(x)\) is expressed by

\[
P_{\text{PoG}}(x) = \phi_A(x) = \frac{A_{\text{po}}(x)}{A_{\text{tot}}} \quad (3.6)
\]

where \(\phi_A(x)\) denotes the sectional porosity, \(A\) is the total area of the cross-section and \(A_{\text{po}}(x)\) is the total area of pores on the cross-section of the cube at distance \(x\). Figure 3.2 is an example of the PoG function. Based on the PoG function, the interfacial transition zone (ITZ) can be distinguished from the bulk zone.

3.2 Pore size estimation

3.2.1 Star volume measure

The stereological technique ‘star volume measure’ (SVM) \[120\] has been proven to be an efficient method to estimate the mean local volume of a very irregular and complex structure (e.g., bones, bone marrow and trabecular), based on a series of 2D sectional images of the structure. The SVM procedure starts by dispersing a number of random points into the investigated phase (e.g., pores) on the 2D images. In each
2D image, these points serve as the nuclei of the ‘stars’; a number of rays (‘intercepts’) are emanated from each point in isotropic directions to the surrounding interfacial surface. The length $l_j$ of each intercept is measured and then is used to obtain the star volume $V^*$ by the third power average:

$$V^* = \frac{\pi}{3N} \sum_{i=1}^{N} l_i^3$$  \hspace{1cm} (3.7)

where $N$ is the total number of generated rays. To obtain a reasonable confidence of the measure, it is necessary to measure 100 to 200 intercepts in as many different directions as possible in the 3D space. Figure 3.3 shows the schematic illustration of using SVM for the cavities of bones [120].

### 3.2.2 Application of star volume measure to 3D virtual pore structure

It is noticed that the investigated porous medium in this study is the virtual one. The 3D version of SVM [121], therefore, can be used to measure directly the local pore volume, instead of the measurement based on the 2D sectional images of a physical specimen. The intercepts $l_j$ in this case are measured with isotropic directions in the 3D space. The volume of the local pore around a typical random point $i$ (nucleus of the star volume) is directly measured by

$$V_i = \frac{4\pi}{3N} \sum_{j=1}^{N} l_j^3$$  \hspace{1cm} (3.8)

and the equivalent diameter of the local pore can be derived, consequently:

$$d_i = 2\left(\frac{\sum_{j=1}^{N} l_j^3}{N}\right)^{1/3}$$  \hspace{1cm} (3.9)
3.2.3 Pore throat estimation

As to the relevance of pore size characteristics to the transport-based properties, it seems more logical to determine the local pore throats. A pore throat in this study is defined as the one that has the smallest area among all cross-sections through a probing random point located in a 3D local pore. A number of trial intersecting planes through the random point with evenly oriented normals are used. The areas of such trial cross-sections are estimated to obtain the one that has smallest area value.

To estimate the area of a cross-section that intersects the 3D local pore at point \( i \), the intercepts \( l_j \) emanated from a random point \( i \) are measured with isotropic directions within the cross-section. The normal of the cross-section can be either in a random or pre-defined direction, depending on the target of the investigation. The area and the equivalent size of the pore throat is given by

\[
A_i = \pi \bar{l_j^2} = \frac{\pi}{N} \sum_{i=1}^{N} l_j^2
\]

\[
d_{thr}^i = 2\sqrt{\frac{\sum_{i=1}^{N} l_j^2}{N}}
\]

where the intercepts \( j \) are restricted to point \( i \).

In this study, 64 trial interesting planes are used to determine the normal of the smallest pore throat through point \( i \). Such trial planes are oriented based on the vectors of 64 ‘general spiral points’ (see Section 2.3.3.1) evenly distributed on the unit sphere’s surface. 8 intercepts are used to roughly estimate the cross-section area for each trial plane. The plane that has the smallest cross-section area is finally used to determine the area and the size of local throat with the proper number of intercepts (e.g., 100-200).

3.2.4 Enhancement of star volume measure

When randomly dispersed in pore space, the nucleus of a star is sometimes located at a corner of an irregular pore with non-convex shape as illustrated in Figure 3.4a. In this case, the estimated volume (area) by SVM is inaccurately estimated. In Figure 3.4a, for example, the area covered by the star (bounded by the dashed line) does not correctly reflect the pore area.

The SVM in this study is enhanced by an iterative process, where the location of the nucleus is iteratively adapted. The process begins by determining the weight centre of the initial star volume, whereupon the weight centre will act as nucleus of the new star in the next iteration (Figure 3.4a); the different locations of the initial and new nuclei may lead to differences in the measured volume. This procedure is iterated until the measured volume converges. Figure 3.4b is an illustration of the SVM estimation after the enhancing process. In each interaction, the new weight centre of
a star, \( \mathbf{x}_c \), is determined based on the lengths of its intercepts and the location of the star’s nucleus, \( \mathbf{x}_s \):

\[
\mathbf{x}_c = \mathbf{x}_s + \frac{3}{4} \sum l_j^4 \mathbf{n}_j \quad \text{for 3D star}
\]

\[
\mathbf{x}_c = \mathbf{x}_s + \frac{2}{3} \sum l_j^3 \mathbf{n}_j \quad \text{for 2D star}
\]

where \( \mathbf{n}_j \) denotes the unit vector expressing the direction of intercepts \( j \).

### 3.3 Random node structuring (RaNoS)

#### 3.3.1 Algorithm

Random node structuring (RaNoS) is a general approach, which can be used for porosimetry of any type of porous medium or paste of packed grains. Figure 3.5 presents a 2-D scheme for RaNoS. It starts by generating with system of random nodes that are uniformly distributed throughout the volume of the porous specimen. Then, the nodes situated in the solid phase are eliminated from further consideration. This yields uniform at random (UR) nodes dispersed inside pores as a detection system of the 3D capillary pore system of the specimen. The next step is a structuring process in which the relationships between nodes are built up by unobstructed straight line segments connecting the nodes.

Two nodes have a ‘direct connection’ when they can be connected together by a straight line that does not intersect with any part of the solid. This initiates the ‘node-clustering’ process during which the connections between all pairs of nodes in the system will be detected; when a discrete node has the direct connection to a node belonging to a cluster, this node will merge into such a cluster. In case two nodes
that belong to two different clusters have the direct connection, such two clusters will merge into a larger one. It is noticed that in the same cluster, there might be pairs of nodes which do not have direct connection. In this case, the connectivity between the two nodes is denoted as an ‘indirect connection’ that is illustrated in Figure 3.5. During the process, the connection detection between two nodes will be relaxed to reduce the computational effort if the detected nodes have been marked to a same group.

Hence, once the clustering process is finished, there are a number of structured clusters of nodes. In each of these clusters, the nodes are mutually connected reflecting the connectivity among pores in the porous specimen. The system of UR nodes can be considered as a nodal-discretized representation of the pore space. Several pore characteristics such as porosity, degree of percolation, pore gradient structure and pore size distribution are assessed based on analysing the structure of such a nodal system, presented in the following section.

The computational algorithms to detect if a node or a line segment collides with a spherical particle as well as an arbitrary polyhedral particle are given in details in [117].

### 3.3.2 Characterization of pore structure by RaNoS

#### 3.3.2.1 Overall porosity

The overall porosity of the container can be statistically calculated by the fraction between the number of nodes located in the pore space and the total number of sampling nodes generated in the whole specimen:
\[
\phi = \frac{n(P)}{n(A)}
\]  
(3.14)

where \( n() \) denotes the total number of elements in a set, and \( P \) and \( A \) denotes the set of the nodes located in the pore space and that of the total sampling nodes generated in the whole specimen, respectively.

### 3.3.2.2 Degree of percolation

The degree of percolation (DOP) of the pore space can be estimated as the ratio of the number of nodes that have a connection to the both sides of specimen to the total number of the UR dispersed nodes.

For assessment of pore connectivity from one side of the specimen to the other side, a number of additional nodes are distributed on the surfaces of both sides of the specimen. These nodes are incorporated in the clustering process. When a cluster of nodes contains at least one node on each of the two opposite surfaces, this cluster represents a percolated pore channel. In estimating DOP, the additional nodes are not taken into account, however. The DOP can be statistically calculated by

\[
\alpha_{per} = \frac{n(P_c)}{n(P)}
\]  
(3.15)

where \( P \) is the set of all nodes in the pore space and \( P_c \subseteq P \) denotes the nodes belonging to the clusters that are connected to the both surfaces of specimen.

### 3.3.2.3 Porosity gradient & determination of ITZ thickness

As above-mentioned, the porosity gradient (PoG) occurs in the ITZ that is characterised by the sectional porosity as a function of distance to the rigid surface as presented in Section 3.1.5. To statistically obtain the section porosity \( \phi_A(x) \) at distance \( x \) to the rigid surface as defined by Eq. (3.6), a thin slice of the specimen with thickness \( \Delta t \) parallel to the rigid surface at distance \( x \) is considered. The sectional porosity can be calculated by the fraction of the total number of nodes located in the pore space on the total number of the sampling nodes generated within this thin slice. Figure 3.6 is an example of the nodes located in pore space within a thin slice of the specimen. The statistic calculation of the sectional porosity can be analytically expressed by

\[
\phi_A(x) = \frac{n\left(p \in P \mid x - \Delta t / 2 \leq d_{RW}(p) < x + \Delta t / 2 \right)}{n\left(a \in A \mid x - \Delta t / 2 \leq d_{RW}(a) < x + \Delta t / 2 \right)}
\]  
(3.16)

where \( d_{RW} \) denotes the distance to the nearest rigid surface of a node.

Going outward from the bulk (middle zone of the specimen), the sectional porosity will start increasing upon approaching the rigid wall. In this study, the border of the ITZ is associated with the point where the porosity of a slice will start exceeding the bulk value by a pre-set threshold of 5%. Because the ITZ border has not been known
yet, a rough value of the bulk porosity can be calculated by averaging the porosity in a middle zone between the two rigid surfaces as:

$$\phi_{\text{bulk}} = \frac{n\left\{ p \in P \mid d_{RW}(p) > L/4 \right\}}{n\left\{ a \in A \mid d_{RW}(a) > L/4 \right\}}$$

(3.17)

where $L$ is the side length of the cube sample. It is noticed that the PoG function formed by the sectional porosity $\phi_A(x_i)$ calculated at different distances $x_i$ is smoothed (fitted) by an inverse power function to eliminate the fluctuation. The fitting function is proposed to have the following form:

$$f(x) = b(x + a)^{-n}(\phi_A(0) - \phi'_{\text{bulk}}) + \phi'_{\text{bulk}}$$

(3.18)

where $b$, $a$, and $n$ are fitting coefficients. The ITZ border is finally determined based on this fitting function. Figure 3.7 is an example of mathematically smoothing the estimated PoG function and determining the ITZ border.

After the ITZ border is determined, the porosity in the bulk zone and that in the ITZ can be separately obtained. For instance, the porosity in the ITZ (or the bulk zone) is calculated as the fraction between the number of random points located in the pore space and that of sampling points generated in the whole ITZ zone (or the bulk zone):

$$\phi_{\text{bulk}} = \frac{n\left\{ p \in P \mid d_{RW}(p) > t_{ITZ} \right\}}{n\left\{ a \in A \mid d_{RW}(a) > t_{ITZ} \right\}}$$

(3.19)

$$\phi_{ITZ} = \frac{n\left\{ p \in P \mid d_{RW}(p) \leq t_{ITZ} \right\}}{n\left\{ a \in A \mid d_{RW}(a) \leq t_{ITZ} \right\}}$$

(3.20)
where $t_{ITZ}$ denotes the ITZ thickness.

### 3.3.2.4 Pore size distribution

To obtain the pore size distribution (PoSD) function of the pore structure, firstly, the size of the local volumetric pore or the pore throat corresponding to each of the UR nodes dispersed in the pore space is assessed by the enhanced SVM presented in Section 3.2.4. Afterwards, the value of the volume-based density PoSD function at size $s$ defined by Eq. (3.5) can be statistically obtained; this value equals the fraction of the total number of nodes having a corresponding pore size within size range $\Delta s$ around $s$ on the total number of nodes located in the pore space, divided by $\Delta s$. The calculation can be expressed by the following equation,

$$
P_{PoSD}(s) = \frac{n \left( \left\{ p \in P \mid s - \Delta s / 2 \leq s_p < s + \Delta s / 2 \right\} \right)}{n(P) \Delta s}
$$

where $s_p$ denotes the corresponding pore size of node $p$. $\Delta s$ in this study is chosen around 0.5-1 µm. The discrete PoSD function is finally obtained with different values of $s_i$.

### 3.3.3 Localized and parallel computing

The RaNoS method focuses on efficiently finding direct connections between neighbouring nodes. The ‘cell method’ [49,122-123] (Figure 3.8) is utilized for this purpose. Each cell contains a list of particles that (partly) overlap with the cell and a list of nodes that are located in the cell. The cells render possible executing localized operations to improve the speed of computation. So, the clustering process is first applied locally in each cell. Thereupon, the clustering process is applied in the
whole simulated space. Moreover, since local clustering processes can be implemented independently and simultaneously, ‘parallel computing processing’, is applied to speed up the computations.

### 3.3.4 Examples

Examples of investigation of the pore characteristics using RaNoS are exerted on the virtual representations of different cement pastes with the characteristics given in Table 3.1. The cubic specimens have a side length of 100 \( \mu \text{m} \). The microstructures have been hydrated using XIPKM presented in Chapter 2. The pore structure of each specimen at various hydration times is investigated.

<table>
<thead>
<tr>
<th>Coded name *</th>
<th>W25F300</th>
<th>W40F300</th>
<th>W40F420</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/c</td>
<td>0.25</td>
<td>0.40</td>
<td>0.40</td>
</tr>
<tr>
<td>Fineness (cm(^2)/kg)</td>
<td>300</td>
<td>300</td>
<td>420</td>
</tr>
</tbody>
</table>

*) The names of cement pastes are coded based on its characteristics

Figure 3.9 shows the dispersed random nodes in the slices of specimens with a thickness of 10 \( \mu \text{m} \).
The porosity gradient (PoG), representing how the porosity measured parallel to the specimen rigid wall varies with the distance to the wall, is shown in Figure 3.10. Figure 3.12 expresses the evolution of the PoG during the hydration process. Based on the smoothed PoG function (using the fitting function as presented in 3.3.2.3), the ITZ thicknesses can be calculated as shown in 3.3.2.3. Based on the determination of ITZ, the overall porosity, the porosity in the bulk zone and the porosity in the ITZ are separately obtained by Eqs. (3.14), (3.19) and (3.20), respectively and shown in Table 3.2. The ITZ porosity is shown to be significant larger, approximately 1.5 times, than the bulk porosity.

Figure 3.9 Visualization of random nodes dispersed in pore space of specimens at 90 days of hydration.

Figure 3.10 Porosity gradient of W25F300 and W40F300 at 90 days of hydration.
Table 3.2 ITZ thickness and porosities of the specimens

<table>
<thead>
<tr>
<th>Coded name</th>
<th>W25F300</th>
<th>W40F300</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITZ thickness (µm)</td>
<td>10.4</td>
<td>14.6</td>
</tr>
<tr>
<td>Overall porosity (%)</td>
<td>8.1</td>
<td>18.6</td>
</tr>
<tr>
<td>Porosity in ITZ (%)</td>
<td>12.4</td>
<td>23.6</td>
</tr>
<tr>
<td>Porosity in bulk (%)</td>
<td>7.6</td>
<td>17.8</td>
</tr>
</tbody>
</table>

Figure 3.11 depicts the sensitivity of the degree of percolation (DOP) on the total number of random nodes dispersed in the pore space (see Eq. (3.15) for the calculation of DOP). The DOP rises at an increasing number of random nodes. It can be explained by the fact that the probability to have ‘direct connections’ between the nodes (Figure 3.5) increases with the higher density of the node system. The conductivities of the pore networks in different specimens can be compared based...
on the sensitivity analysis. At the density of 0.1 node/µm$^3$ as shown in Figure 3.11a, for instance, the DOP of the specimen with w/c = 0.25 equals zero, whereas the DOP of the specimen with w/c = 0.4 almost equals 1. Moreover, the DOP of the specimen with w/c = 0.4 is highly sensitive at low node density, presented by the deep gradient of the DOP function in Figure 3.11a. Therefore, it can be inferred that the conductivity of the pore network of the specimen with w/c = 0.4 is much higher than that with w/c = 0.25. Similarly, it can be observed that the higher cement fineness lead to lower connectivity of the pore space.

The system of random nodes can be also considered as a representative transport conductor to fully fill the pore space; the denser density the conductor has, the higher the conductivity of the porous material is.

The local volumetric (3D) pore sizes and throat sizes (smallest area cross-section) at the random nodes in specimen W40F300 are estimated by the enhanced SVM (see Section 3.2.4) and are characterised by the pore size distribution (PoSD) functions, as shown in Figure 3.13. The functions show that the sizes of the pore throats are considerably smaller than those of the 3D pores; the distribution mode (i.e., the most common value of the frequency) of the throat sizes is approximately 3.4 µm whereas that of the 3D pores is around 7.4 µm.

The anisotropy of the throat size in the ITZ of specimen W40F300 is demonstrated in Figure 3.14; the throat sizes estimated in the planes orthogonal to the rigid surfaces are smaller than those parallel to the rigid surfaces. This anisotropic structure of the pore size is caused by the phenomenon of packing particles in a container with two opposite rigid surfaces, whereby the particles are packed more tightly in the direction (x-direction) perpendicular to the rigid surfaces than in the others directions orthogonal to the x-direction.

![Figure 3.13 Comparison in size distribution between 3D pores and pore throats of specimen W40F300.](image-url)
The comparison cases in PoSD for different w/c ratios and cement fineness are shown in Figure 3.15. Based on the PoSD functions, it can be inferred that the throat sizes of the specimen with w/c = 0.25 are significantly smaller than those with w/c = 0.4 because of the smaller porosity. At the almost same porosity (≈18%), the specimen with higher cement fineness (W40F420) has throat sizes much smaller than the specimen with lower cement fineness (W40F300). This difference can be explained by that the spacing between coarse particles is well filled with the fine ones in the high fineness paste which results in the smaller pore sizes.

Figure 3.16 shows the pore size distribution of the simulated paste W40F420, compared to that of a physical paste carried out by Lange [13] using image analysis techniques. It is noticed that only large capillary pores ranging in size from 0.1 μm$^2$ to about 300 μm$^2$ are observed due to image resolution limitation. The difference between the two curves in Figure 3.16. can be explained by the assumption of
spherical particles as well as idealized spherical layers of hydration products in the model paste, probably leading to coarser pore sizes than those in the physical paste.

3.4 Summary

A novel efficient porosimetry applied to virtual presentations of porous materials is presented, which combines reliability and efficiency. The pore structure is configured based on a system of random nodes dispersed uniformly at random (UR) in the pore space, or in other words, the pore space is represented by a system of UR nodes. Several techniques are presented to characterise the parameters of pore structure by statistically analysing the configuration of the system of UR nodes. Moreover, the system of UR nodes can also represent a transport conductor to fill up the pore space, whereby the higher density leads to the higher connectivity of the porous medium.

The well-known stereological technique – star volume measure (SVM) – is employed to estimate directly the sizes of the volumetric local pores as well as pore throats which are more relevant to transport properties of the pore space. Furthermore, the SVM is enhanced for a more efficient assessment of irregular pores.

The existence of ITZ in the exampled specimens of cement pastes has been demonstrated in the aspect of the porosity gradient (PoG). Based on a PoG function, the ITZ thickness can be calculated in an analytical way. The examples also present the comparisons in pore size distribution between virtual cement pastes with different w/c as and grain fineness as well as between ITZ and bulk. The sensitivity analysis of degree of percolation has been shown as a representative transport property.
Chapter 4 Permeability estimation for a virtual porous medium*

The permeability is the most important property concerning the transport-based durability of porous materials. Experimental assessment of the hydraulic permeability of porous materials is a challenging task, especially for materials revealing long-term microstructural evolution such as in the case of cementitious materials. The self-sealing effect [18], which occurs during water permeability test, usually leads to high errors in the measured results. In fact, this phenomenon causes dissolution and precipitation of ions along the flow paths, continuing hydration by water saturation, flow path blocking by movement of loose particles under high pressure and swelling of the CSH gel due to re-saturation. This leads to significant changes in the pore structure. Moreover, this experimental approach is very complex and laborious and requires expensive instrumentation.

As an alternative, several analytical models have been developed to predict the permeability of porous media in an indirect way based on the pore characteristics. Furthermore, the permeability can also be predicted with numerical models that directly solve the flow at pore scale through the virtual representation of porous media. The models for predicting the permeability have been reviewed in Section 1.4.1 of this thesis. This chapter presents two computational methods to predict the macroscopic permeability of porous materials. These methods estimate directly the water flow under a pressure gradient at pore-scale through the 3D virtual representations of the material. The first method is applicable to virtual porous specimens that are characterised by a voxel-based system. FEM is used to solve the saturated, slow and incompressive flow that is characterised by the linear Stokes problem, where each voxel of pore phase is used as a 3D (finite) element. The second method is based on a porosimetry named ‘Double-Random Multiple Tree Structuring’ (DRaMuTS). DRaMuTS is an enhanced version of the RaNoS porosimetry method presented in Chapter 3, whereby the topology of the pore structure is efficiently explored with a system of concurrent virtual trees that grow and branch randomly in pore space. An equivalent network of hollow non-circular cylindrical tubes is derived from the geometrical pore characteristics and the tree

* Parts of this chapter were published elsewhere (Stroeven et al. [106])
structure. The flow through this tube network is solved in a much more efficient way as compared to the FEM-based method.

### 4.1 Permeability

Permeability characterizes a porous medium on the aspect of the flow rate of a liquid through it under a saturation condition. The relation of the macroscopic permeability to the flow rate in a porous medium can be expressed by Darcy’s law,

\[
q = -\frac{k}{\mu} \nabla P
\]  

(4.1)

where \( q \) is the flux vector (discharge per unit area and per unit time, m/s), \( k \) (m²) denotes the second-order tensor of permeability, \( \nabla P \) (Pa/m) is the pressure gradient and \( \mu \) (Pa.s) is the dynamic viscosity that equals 0.001 (Pa.s) for water. For a specimen of porous material with cross section \( A \) and length \( L \), the permeability in the direction along the length of the specimen can be obtained by

\[
k = -\frac{\mu Q L}{A \Delta P} \quad \text{(m}^2) \quad \text{or,}
\]

\[
k_h = -\frac{Q L}{A \Delta h} \quad \text{(m} / \text{s})
\]

(4.2) \hspace{1cm} (4.3)

where \( k \) and \( k_h \) denote the intrinsic and hydraulic permeability coefficients, respectively. The intrinsic permeability is dependent only on the geometrical characteristics of the pore structure, whereas the hydraulic permeability depends further on the properties of the moving fluid. \( Q \) (m³/s) is the total volumetric inlet (outlet) flow rate through the specimen. \( \Delta P \) (Pa) and \( \Delta h \) (m) denote the pressure difference between the inlet and outlet ends of the specimen and the drop in hydraulic head, respectively. In the case the velocity field of flow at pore scale through a representative specimen of porous medium is solved, the homogeneous permeability of the medium can be determined by

\[
k_r = -\frac{\mu \langle u_r \rangle L}{\Delta P} \quad \text{(m}^2)
\]

\[
k_{r,h} = -\frac{\langle u_r \rangle L}{\Delta h} \quad \text{(m} / \text{s})
\]

(4.4) \hspace{1cm} (4.5)

where \( r \) denotes the direction \( (r = x, y, z) \) and \( \langle u_r \rangle \) is the averaged velocity. The averaged velocity can be obtained by either volume averaging or area averaging on the inlet (outlet) surface.

### 4.2 Stokes mixed FEM approach

#### 4.2.1 Governing equations and weak forms

Since the pore-solid interface area is large for porous media, the saturated flow through it can be assumed to be slow, stable and incompressible. Neglecting the
body forces (e.g., gravity), the flow can be characterized by the linear Stokes equations:

\[-\mu \Delta u^r + \frac{\partial p}{\partial x^r} = 0\]  
\[\nabla \cdot u = 0\]

with \(u\) and \(p\) denoting the velocity vector and pressure field, respectively, and \(r = 1, 2, 3\) indicating the spatial dimension. The latter equation expresses the continuity or incompressibility constraint. The equations (4.6) and (4.7) are multiplied by weight functions \(\varphi\) and \(\Psi\) and integrated over the domain to derive the weak forms of the Stokes equations respectively,

\[\int_\Omega \left(-\mu \Delta u^r + \frac{\partial p}{\partial x^r}\right) \varphi d\Omega = 0\]  
\[\int_\Omega \nabla \cdot u \psi d\Omega = 0\]

where \(\Omega\) is the 3D domain of the problem bounded by the boundary \(\Gamma\). By applying the Gauss divergence theorem, Eq. (4.8) becomes:

\[\int_\Omega \mu \nabla u^r \nabla \varphi d\Omega - \int_\Omega p \frac{\partial \varphi}{\partial x^r} d\Omega - \int_\Gamma \mu \frac{\partial u^r}{\partial n} \varphi d\Gamma + \int_\Gamma p \varphi n^r d\Gamma = 0 .\]  

4.2.2 Boundary conditions

The problem is considered for the case whereby the domain \(\Omega\) is contained within a parallelepiped space. It is assumed that the boundary of the domain is subdivided into the following parts: fixed wall \(\Gamma_d\) (Dirichlet), prescribed pressure \(\Gamma_p\) and periodic boundaries \(\Gamma_{pe1}\) and \(\Gamma_{pe2}\) as illustrated in Figure 4.1. With the assumption of no slip at the fixed walls, the boundary conditions at \(\Gamma_d\) are expressed as

\[u = 0 \text{ and } \varphi = 0 \text{ on } \Gamma_d\]  

(4.11)
which eliminates the two latter terms in (4.10) at the Dirichlet boundary. The periodic boundary conditions of the domain are given by

\[
\begin{align*}
\mathbf{u}|_{\Gamma_{pe1}} &= \mathbf{u}|_{\Gamma_{pe2}}, \\
p|_{\Gamma_{pe1}} &= p|_{\Gamma_{pe2}}.
\end{align*}
\] (4.12)

As a result, also the two latter terms in Eq. (4.10) can be eliminated. It is difficult to include explicitly a boundary condition where pressure is prescribed [124-125]. In order to consider the boundary condition where the pressure is prescribed, the following condition is used:

\[-\mu \nabla \mathbf{u}. \mathbf{n} + p \mathbf{n} = p_o(\mathbf{x}) \mathbf{n}.\] (4.13)

Applying this condition for a linear boundary that is perpendicular to a coordinate axis yields

\[-\mu \frac{\partial \mathbf{u}}{\partial n} + pn' = p_o(\mathbf{x})n'.\] (4.14)

and it can be seen that in case of \( \frac{\partial \mathbf{u}}{\partial n} = 0 \) (e.g., at the inlet surface perpendicular to the direction of stable flow), \( p_o \) is exactly equal to the pressure applied on the boundary. Imposing the above-mentioned boundary conditions lead to the simpler form of Eq. (4.10)

\[
\int_{\Omega} \mu \nabla \mathbf{u}. \nabla \varphi d\Omega - \int_{\Omega} p \frac{\partial \varphi}{\partial x} d\Omega = - \int_{\Gamma_p} p_n' \varphi d\Gamma
\] (4.15)

4.2.3 Mixed FEM Discretization

The Stokes problem consists of two different types of unknowns, i.e., velocity and pressure. To solve the problem by FEM, different basic functions are employed for the different unknowns, which is well known as a mixed FEM. Using the standard FEM Galerkin method, the approximations of \( \mathbf{u} \) and \( p \) can be expresses by

\[\text{Figure 4.1} \quad 2D \text{ schematic illustration of domain and boundary conditions.}\]
Permeability estimation for a virtual porous medium

\[ u'(x) \approx u_h'(x) = \sum_{i=1}^{n} u_i' \phi_i(x) \]  \hspace{1cm} (4.16)

\[ p(x) \approx p_h(x) = \sum_{i=1}^{m} p_i \psi_i(x) \]  \hspace{1cm} (4.17)

where \( \phi_i(x) \) and \( \psi_i(x) \) are the basic functions for the velocity and the pressure corresponding to node \( i \), \( n \) and \( m \) are the numbers of discretized nodes in each direction for velocity and pressure respectively, and \( u_i' \) and \( p_i \) denote the values of fields \( \phi_i(x) \) and \( \psi_i(x) \) at node \( i \). Taking \( \phi = \phi_i(x) \) and \( \psi = \psi_i(x) \) and substituting (4.16) and (4.17) into (4.9) and (4.15) yield the discrete formulation of the problem as follows,

\[ \sum_{j=1}^{n} u_j' \int_{\Omega} \mu \nabla \phi_i \cdot \nabla \psi_j d\Omega - \sum_{j=1}^{m} p_j \int_{\Omega} \frac{\partial \phi_i}{\partial x^r} \psi_j d\Omega = -\int_{\Gamma_p} p_i \nu \phi_i d\Gamma \quad i = 1, \ldots, n \] \hspace{1cm} (4.18)

\[ \sum_{r=1}^{3} \sum_{j=1}^{n} \int_{\Omega} \frac{\partial \phi_i}{\partial x^r} \psi_j u_j' d\Omega \quad i = 1, \ldots, m . \] \hspace{1cm} (4.19)

This linear system can be written in a matrix form as:

\[ \begin{bmatrix} N_{(3n \times 3n)} & -Q_{(3n \times m)} \\ Q^T_{(m \times 3n)} & 0_{(m \times m)} \end{bmatrix} \begin{bmatrix} v_{(3n \times 1)} \\ p_{(n \times 1)} \end{bmatrix} = \begin{bmatrix} b \end{bmatrix} \] \hspace{1cm} (4.20)

where

\[ N = \begin{bmatrix} N^1_{(n \times n)} & 0 & 0 \\ 0 & N^1_{(n \times n)} & 0 \\ 0 & 0 & N^1_{(n \times n)} \end{bmatrix} \] \hspace{1cm} (4.21)

\[ Q^T = \begin{bmatrix} Q^1_{(n \times m)} \\ Q^2_{(n \times m)} \\ Q^3_{(n \times m)} \end{bmatrix} \quad b^T = \begin{bmatrix} b^1_{(n \times 1)} \\ b^2_{(n \times 1)} \\ b^3_{(n \times 1)} \end{bmatrix} \] \hspace{1cm} (4.22)

or

\[ Nv - Qp = b \] \hspace{1cm} (4.23)

\[ Q^T v = 0 , \] \hspace{1cm} (4.24)

where the elements of \( N^1 \), \( Q^T \) and \( b^T \) are given by

\[ N^1_{ij} = \int_{\Omega} \mu \nabla \phi_i \cdot \nabla \phi_j d\Omega \] \hspace{1cm} (4.25)
\[ Q'_{ij} = \int_{\Omega} \frac{\partial \phi_r}{\partial x^i} \Psi_j d\Omega \]  
(4.26)

\[ b'_i = -\int_{\Gamma_p} p_\nu \nu^i \varphi_i d\Gamma \]  
(4.27)

and \[ \mathbf{v} = (u_1^1, \ldots, u_n^1, u_1^2, \ldots, u_n^2, u_1^3, \ldots, u_n^3)^T \]  
(4.28)

\[ \mathbf{p} = (p_1, \ldots, p_n)^T \]  
(4.29)

4.2.4 Admissible element

Not any approximation of velocity can be mixed with any approximation of pressure when solving the Stokes problem. The selected basis functions of velocity and pressure should satisfy the compatibility condition for the velocity-pressure mixed method, i.e., the well-known Babuska-Brezzi (BB) condition \([126-127]\). This condition is, however, rather abstract and in practise it is hard to check. The 3D cubic element named ‘enriched-restricted triquadratic velocity-constant pressure’ (R$^2_T$-$P_0$), which has been proven to satisfy the BB condition and to be an efficient 3D element for incompressive flows \([128]\), is employed in this study. The nodes for velocity approximation are located at the vertices, the edge middles and the face centres of the element; each vertex node includes three velocity components (degrees of freedom) in the three directions, each mid-edge node includes two velocity components that are perpendicular to the edge and each mid-face node includes only one velocity component that is normal to the face (Figure 4.2). The approximate pressure is constant in the domain of the element (discontinuous approximate pressure field) with only one internal node situated at the element’s centre.
4.2.5 Solving the linear equation system

Basically, the system of linear equations of Eqs. (4.23) and (4.24) can be solved directly. However the absence of pressure unknowns in continuity equations makes it difficult to solve the problem [124,129], especially for porous media with complex boundaries. Hence, the so-called discrete penalty method [124,129] is employed to solve the system of linear equations in an indirect way, in which the continuity is perturbed by a term $\varepsilon M P$, where $\varepsilon$ expresses a small value and $M$ is the so-called pressure mass matrix defined by the following elements

$$M_{ij} = \int_{\Omega} \psi_i \psi_j d\Omega.$$ \hspace{1cm} (4.30)

Hence,

$$Q^T v + \varepsilon M P = 0$$ \hspace{1cm} (4.31)

or

$$P = -\frac{1}{\varepsilon} M^{-1} Q^T v.$$ \hspace{1cm} (4.32)

Substituting $P$ in Eq. (4.32) into Eq. (4.23) gives

$$\left( N + \frac{1}{\varepsilon} QQ^T \right)v = b.$$ \hspace{1cm} (4.33)

Therefore, nodal velocity $v$ can be computed separately from Eq. (4.33), whereupon $P$ is then computed from Eq. (4.32). The difficulty in solving these systems of equations may come from calculating the inverse matrix $M^{-1}$. Since the use of the $R^+_2 - P_o$ elements gives a discontinuous approximate field of pressures, fortunately, the mass pressure matrix $M$ is a unity matrix and thus its inverse can be easily obtained.
4.2.6 Examples

4.2.6.1 Validation for simple cases

The FEM Stokes solver for steady, slow and incompressible flows is validated by comparing the numerical results to analytical ones in two simple cases: the laminar flow between two parallel plates and the flow in a circular pipe. The considered volume is contained in the region, in which the length (in flow direction), the distance between the two plates and the diameter of pipe are all 1 unit. The pressure difference is set as 1 unit by assigning the pressure values 1 and 0 at the two heads of the container. The dynamic viscosity of the liquid is assumed to be 1 unit. The velocity in longitudinal direction is calculated by

\[ u = -\frac{1}{2\mu} \frac{dp}{dx} (H - z) \quad \text{for flow between two plates} \]  

\[ u = -\frac{1}{4\mu} \frac{dp}{dx} (R^2 - r^2) \quad \text{for flow in the circular pipe} \]

Where \( \frac{dp}{dx} \) denotes the pressure gradient, \( H \) is the distance between the two plates and \( R \) is the radius of the circular pipe. The plots shown in Figure 4.3 and Figure 4.4 reveal very good agreement between the numerical and the analytical results.

![Figure 4.3](image)

*Figure 4.3 Flow between two parallel plates: (a) pressure gradient and (b) flow velocity in longitudinal direction*
4.2.6.2 Virtual cement pastes

The Stokes FEM solver is applied to investigate the water permeability of virtual representations of the matured cement described in Section 3.3.4 of Chapter 3. The pore features (i.e., porosity and ITZ thickness) of the specimens are shown in Table 3.2. The pressure gradient is applied to the specimens by prescribing the pressure of 1 and 0 Pa at the bottom and top surfaces of each specimen, respectively. All specimens are discretised by 150x150x150 voxels. The voxels representing the pore phase are used to configure the cubic finite elements as presented in Section 4.2.4.

The velocity $V_z$ (bottom-top direction) averaged in thin slices parallel to the rigid wall is depicted by Figure 4.5, expressing how the velocity varies as function of the distance to the rigid wall. The velocity is averaged by volume within a slice with the thickness equal to the voxel size. It can be seen that the velocity is higher in the ITZ than in the bulk. The velocity is shown to be much smaller for the lower w/c
(comparing W25F300 vs. W40F300) and for the higher cement fineness (comparing W40F300 vs. W40F420). The difference in velocity between the bulk zone and ITZ is more significant at the lower w/c and at the higher cement fineness, especially in W25F300.

The intrinsic permeability values of the specimens are calculated and shown in Table 4.1. For each specimen, there are three different values of estimated permeability: (1) the overall permeability of the whole sample, coupling the ITZ and bulk zone, (2) the permeability of the bulk zone and (3) the permeability of the ITZs. Figure 4.6 shows these estimated values for the three specimens. The permeability is shown to be larger in the ITZ than in bulk. The permeability is also revealed to be much smaller for the lower w/c and for the higher cement fineness. The difference in permeability between the bulk zone and ITZ is observed to be more significant for the lower w/c and for the higher cement fineness.

<table>
<thead>
<tr>
<th>Coded name</th>
<th>W25F300</th>
<th>W40F300</th>
<th>W40F420</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coupled ITZ+bulk</td>
<td>1.453e-16</td>
<td>3.562e-15</td>
<td>1.608e-15</td>
</tr>
<tr>
<td>Bulk</td>
<td>9.516e-17</td>
<td>3.060e-15</td>
<td>1.265e-15</td>
</tr>
<tr>
<td>ITZ</td>
<td>3.043e-16</td>
<td>6.194e-15</td>
<td>3.120e-15</td>
</tr>
</tbody>
</table>

4.3 Double-Random Multiple Tree Structuring (DRaMuTS)

An approach to solve slow, stable and incompressible flow through porous materials that is based on a novel porosimetry denoted ‘Double-Random Multiple Tree Structuring’ (DRaMuTS) is presented in this section. The porosimetry is in fact an extension of RaNoS (Chapter 3). This method is enhanced by a system of structured virtual trees that grow randomly in the pore space. Based on the configuration of the virtual trees, the percolated pores are converted into an equivalent network of cylindrical tubes, whereby the flow can be solved in a much cheaper way than using Stokes FEM method.
Before constructing the network of tubes, firstly, the porosity aspects of DRaMuTS will be presented in Section 4.3.1. The pore structure is explored and characterised by randomized structures that are built incrementally in two stages. In the first stage, the porous medium is iteratively invaded by a system of growing branches (to form trees), the growth of which is configured by an algorithm taken from robotics. In the second stage, a system of uniform at random (UR) nodes dispersed in the pore space is generated (as presented in the RaNoS method) to statistically investigate the pore features with the aid of the system of virtual trees.

4.3.1 Algorithm

4.3.1.1 Generation of tree system (1st stage)

Inspiration for the present approach is derived from the so called ‘rapidly-exploring random tree’ (RRT) algorithm in robotics developed in LaValle and Kuffner [130]. This efficient path planning algorithm pursues finding a way from point A to point B, avoiding any collision with dispersed obstacles. Path planning is implemented by generating a ‘virtual tree’ system that includes sets of nodes (‘vertices’) and branches (‘edges’) that connect pairs of nodes (like branches of real trees). This tree grows incrementally and randomly in 3D. The expansion of the tree is illustrated in Figure 4.7. The generation procedure of a new branch (new vertex) starts by generating a random point (point 4 in Figure 4.7). The random point is then moved in a straight direction towards the nearest existing vertex (5), thereby determining a line segment (between (5) and (6) or between (5) and (7)) having a length equals the predefined maximum incremental distance, $\varepsilon$. Next, a check for collision with an obstacle is executed. No collision (7) leads to addition of a new vertex and a segment to the tree. At collision (6), a new random point is generated and the procedure is repeated until a new point without collision is achieved. The expansion procedure is repeated until there is a vertex that can connect to the destination (point A). The path way is then defined by extracting from the tree system a chain of tree edges connecting the starting points and the destination point. Figure 4.9 illustrates a path planning by the RRT algorithm. The application of RRT in practise can be demonstrated by the way a robot moves to a destination in a warehouse, avoiding

![Figure 4.7 Expansion of tree system by RRT algorithm.](image-url)
shelves as obstacles the map of which has been configured already in the robot’s memory.

The RRT algorithm can also be used for exploration of the pore structure. However, the RRT needs significant upgrading for porosimetry applications. The upgrading of RRT consists of two modifications. Firstly, since a large number of trials may be involved by the original RRT algorithm, generation of the complete tree system in a highly complex and tortuous pore space would be laborious. In the present approach, therefore, instead of generating a new point once collision of the generated random point (4) is detected with an obstacle, a line segment is created between the new point (4) and the nearest vertex (5) as in Figure 4.8. The intersections (6) between the line segment (4-5) and the obstacles are then detected. Next, the new point (7) that located between the nearest intersection and the nearest vertex (5) then becomes a new vertex. The location of the new point is defined by a ratio (e.g., 0.5) relative to the length of the segment between nearest intersection and the nearest vertex. This excludes making iterations, because there is always one new vertex in the generation

**Figure 4.8**  Enhanced RRT algorithm for expansion of tree system.

**Figure 4.9**  Example of path planning by RRT algorithm. The tree grows in the whole space avoiding the obstacles. The red curve extracted from the tree marks the found way.
process. This speeds up the generation of the whole tree system and constitutes therefore a significant improvement of the efficiency of the RRT algorithm.

Secondly, exploration by a single tree system seems not to be appropriate in porosimetry; many channels constituted by percolated pores getting through a porous specimen exist concurrently. Parallel development leads to the so called ‘multiple-tree’ network. Herein, tree systems grow incrementally from a set of different points referred to as ‘seeds’. The seeds are sowed in local pores (2D pore sections) on both opposite surfaces of the specimen in order to possibly obtain a tree system getting through the specimen (e.g., from bottom to top surface). It is noticed that there is only one seed for a local pore on a surface as illustrated in Figure 4.10. Additionally, efficiency can be improved by sowing the seeds in local pores that are located inside the specimen.

Once the predefined total number of generated tree branches is obtained, the generation procedure is complete. There is a system of separate trees growing from the different seeds and spanning the full pore space of the specimen. Thereafter, the connectivity between the tree systems is checked based on the ‘direction connections’ between the vertices that presented in the algorithm of RaNoS (Section 3.3.1). The different trees that can be connected together will merge into a single cluster (group) of trees. Based on these tree groups, the trees are then classified into different categories. Firstly, the trees are separated into ‘percolated’ (connected) versus ‘isolated’ trees. The ‘percolated trees' are defined as ones belonging to a tree group that can be connected to both sides (e.g., bottom and top surfaces) of the specimen. This tree group should contain at least two trees: one growing from a seed located on the bottom surface and the other one growing from a seed located on the top surface. The remaining trees are defined as 'isolated trees'. Secondly, the ‘percolated trees’ are separated into ‘main trunks’ and ‘dead-end braches’. The ‘main trunks’ represent the tracks of the direct paths that are the pore channels significantly contributing to flow through the specimen. The procedure of extracting the ‘main trunks’ from the ‘percolated trees’ will be presented later in Section 4.3.2.
4.3.1.2 Generation of UR nodes (2nd stage)

It is noticed that the tree vertices are distributed randomly but not uniformly as a result of improvements to speed up exploration of pore space. So, these nodes cannot be used to analyse the pore characteristics. For that purpose, a second system of UR dispersed nodes is generated in a similar way as in RaNoS. This random system of nodes, together with the tree system, expresses the ‘double-random’ in the name of the approach. Based on the connectivity to the different types of trees generated in the 1st stage, the UR nodes are also classified into corresponding categories (i.e., ‘isolated’ vs. ‘percolated’, ‘main channels’ vs. ‘dead-end branches’). Such categories of nodes represent the different types of pores and can be used to statistically estimate the fractions relating the characteristics of pore structure (e.g., degree of percolation and the main path fraction). It is noticed that separating between main trunks and dead-end branches is a new feature of DRaMuTS and is impossible in RaNoS.

4.3.2 Extraction of main trunks from percolated trees

4.3.2.1 Algorithm

As introduced in the previous part, the ‘main trunks’ represent the tracks of the direct paths between opposite sides of the specimens, e.g., top and bottom surfaces of a cube specimen. In the other words, these main trunks can be considered as the skeleton of the main pore channels for flow.

As above-mentioned, a group (cluster) of percolated trees consists of a number of trees that can be connected to both sides of the specimen. Let us consider two

![Diagram](image)

**Figure 4.11** Main trunk extracted from the tree system in a 2D specimen of circular particles. Seeds are sowed on top and bottom edges and on internal layers (horizontal lines).
adjacent trees that are connected to each other. Herein, the main trunk extracted from the two trees is defined as a chain of tree edges that directly connects the seeds of the two trees. Since the two trees expand and branch fully in the pore space from the two seeds, the two seeds can be connected to each other by a number of different paths. Therefore, the extracted main trunk is defined uniquely as the one which has the highest hydraulic conductance. For each pair of connected trees, only one main trunk is extracted, which results in a system of main trunks going through the specimen from bottom to top surface. Figure 4.11 is an example of the main trunks extracted from a system of trees in a 2D specimen of circular particles.

4.3.2.2 Main trunk smoothing

As the trees branch randomly in the pore space, the main trunks may have a zig-zag shape even if they traverse a rather smooth channel. Therefore their total length perhaps exceeds the actual flow length of the main pore channels. In this study, the main trunks are therefore geometrically smoothed to decrease their total length to, as closely as possible, the actual length of main pore channels. Two algorithms for smoothing named 'mid-point' and 'end-point' smoothing are implemented. Both methods are illustrated in Figure 4.12.

In the first one, the line segments between middle points of two consecutive original lines are checked whether they are free or obstructed (the method is referred to 'mid-point' or MP). If a line segment is unobstructed, it will replace the second half and the first half of the two corresponding lines. If a detecting line segment is obstructed, there is no change.

In the second one, the line segments between first end and second end of two consecutive original lines are checked whether they are free or obstructed (the method is referred to 'end-point' or EP). If a detecting line is unobstructed, it will replace the two corresponding lines. If a detecting line is obstructed, there is no change.

![Figure 4.12 Illustration of main trunk smoothing.](image-url)
The smoothing procedure is iterated a number of times until the total length of the main trunks is unchanged. With the first one, the trunk will be smoother after each iteration. This type of smoothing decreases the difference between angles of two consecutive edges of a main trunk. With the second one, a trunk will be straighter after each iteration. Figure 4.13 depicts the decrease in length of the total main trunks in a cube of matured cement paste, using the smoothing algorithms separately and the efficiency by combining them for main trunks generated in a specimen of matured cement paste. It is noticed that the MP algorithm derives only from elimination of the natural fluctuation of the tree system. Whereas, though giving dramatically shortening the total length of the tree system in a few interactions, the...
Permeability estimation for a virtual porous medium

reduction by EP algorithm is quickly marginal because of the growing obstacle of particles during straightening the tree system. Hence, the inferiority of the combined algorithm derives from straightening by EP as much as possible the tree system successively after a number of MP interactions. Figure 4.14 shows the main trunks of the 2D particle paste before and after smoothing.

4.3.3 Flow estimation by ‘tube model’

4.3.3.1 Construction of ‘tube model’

The percolated pore system of a specimen of porous materials herein is converted into a network of linked cylindrical tubes to represent flow through the specimen and therefore water permeability. It is assumed that pore channels that are tracked by the main trunks mainly contribute to flow, whereas the other pores can be neglected. The network of equivalent tubes can be constructed along the main trunks. In other words, the main trunks can be considered as the skeleton axes of the tube network. The equivalent tube diameters along the main trunks are measured by using the enhanced SVM (Section 3.2.4) to estimate the sizes of pore throats on the planes perpendicular to the main trunks. The volumetric flow, $Q_{ij}$, in a tube segment with a pressure difference between the two ends ($i$ and $j$) can be expressed by

$$Q_{ij} = G_{ij} (p_i - p_j) \quad (4.36)$$

where $G_{ij}$ denotes the hydraulic conductance of the tube segment and $p_i$ and $p_j$ are the applied pressures at the two ends of the segment. At each node $i$ that connects a number of the tube segments, the mass conservation law of flow gives

$$\sum_{j=1}^{n_i} Q_{ij} = 0 \quad (4.37)$$

where $n_i$ is the total number of tubes having node $i$ as the common end, and $j$ denotes the other ends of the tube. Substituting Eq. (4.36) into Eq. (4.37), a set of algebraic linear equations with nodal pressures as unknowns is obtained. Applying the prescribed pressures at the nodes (tube ends) located at the bottom and top surfaces of the specimen, the nodal pressures are determined by solving the linear system of equations. The flow rate in each tube and thus the total outlet (inlet) flow rate can be calculated, whereby the average velocity of flow and therefore permeability can be estimated by Eq. (4.4) or (4.5).

4.3.3.2 Estimation of hydraulic conductance

It is noticed that the tubes in this model are not cylindrical; the cross-section of a tube segment can vary along its length. To obtain the hydraulic conductance $G$ of a tube segment, therefore, the hydraulic conductance of the varying cross-section need to be determined. The overall conductance $G$ of a tube segment of length $L$, with the cross-section varying along its, is given by [131]:

$$G = \int_{A(x)} \frac{dA}{dx} L \quad (4.38)$$

where $A(x)$ is the cross-sectional area at a distance $x$ from one end of the segment.
where \( \langle \bullet \rangle \) denotes the average value along the length of the tube. Such average value can be obtained over a number of discretized points along the length of the tube. The conductance of a cross-section, \( C \), is related to the volumetric flow rate \( Q \) and the pressure gradient \( \Xi = \partial p/\partial x \) by the following equation

\[
Q = C \frac{\partial p}{\partial x} = C \Xi . \tag{4.39}
\]

For an ideal circular cross-section, the conductance can be derived from the Hagen–Poiseuille’s equation for a parallel flow of axial symmetric and parabolic velocity distribution in a circular pipe (with \( u_{\text{max}} \) at the centre):

\[
C_{\text{cir}} = \frac{\pi D^4}{128 \mu} \tag{4.40}
\]

where \( D \) is the diameter of the circular section. However, the cross-sections of capillary pores in porous media, even originating from spherical particles, are generally not circular but very irregularly shaped. The influence of the shape factor that represents the irregularity of the cross-section should therefore be taken into account for the estimation of cross-section conductance. Patzek and Silin [132] investigated conductance of non-circular cross-sections, \( i.e., \) triangular, rectangular and elliptic shapes, in which the cross-sectional conductance is shown to be proportional to a shape factor of the cross-section. The shape factor in such investigation is expressed through the dimensionless Mason and Morrow’s ‘shape factor’ [133],

\[
Sh = \frac{A}{P^2} \tag{4.41}
\]

where \( A \) and \( P \) denote the cross-sectional area and the perimeter, respectively. The cross-sectional conductance in that research is expressed by a dimensionless term defined by

\[
\tilde{C}_{\text{cir}} = \frac{C \mu}{A^2} \tag{4.42}
\]

where \( C \) can be obtained through the volumetric flow rate \( Q \) by Eq. (4.39). The volumetric flow rate through a cross-section is determined by analytically solving the Poisson equation (a reduced form of the Stokes equation (Eq.(4.6)):

\[
\nabla^2 u = \frac{1}{\mu} \Xi \tag{4.43}
\]

where \( u \) denotes the flow velocity in the direction normal to the cross-section.

In this study, Eq. (4.43) is solved by FEM to obtain the velocity field \( u \) with the Dirichlet condition at the boundary of the cross-section. The velocity is integrated
over the cross-section area to obtain the volumetric rate and therefore the hydraulic conductance. Figure 4.15 is an example of the velocity field in the cross-section of a pore in simulated cement paste; the geometrical configuration of the pore section is obtained by the enhanced SVM. Figure 4.16 shows the relation between the dimensionless conductance and the shape factor of a cross-section of pore in a matured cement specimen. This relation is compared to those of triangular and quadrilateral cross-sections, the side lengths of which are randomly configured. It can be seen that all values of conductance as well as shape factor $Sh$ are smaller than those of the circular section, i.e., $\tilde{C}_{cir} = 1/8\pi \approx 0.04$ and $Sh_{cir} = 1/4\pi \approx 0.08$.

To obtain the conductance of all equivalent tubes, the cross-section hydraulic conductance can be calculated at the pore throats along the main trunks. However, solving the flow by FEM at every pore throat would be not practical. In this study, therefore, the influence of shape factor on conductance of an individual porous specimen is integrated statistically; the dimensionless conductance is estimated by

\[ C_{\text{est}} = \frac{1}{\pi} \int_{\Omega} C(\Omega) \cos(\theta) \, d\Omega, \]

where $C(\Omega)$ is the dimensionless conductance for a particular cross-section and $\theta$ is the angle between the normal to the cross-section and the direction of the flow. The integration is performed over the entire pore space $\Omega$. The shape factor $Sh$ is related to the cross-sectional area $A$ and the length $L$ of the pore by

\[ Sh = \frac{A}{\pi L^2}. \]

The dimensionless conductance $\tilde{C}$ is then calculated as

\[ \tilde{C} = \frac{C}{\mu L}, \]

where $\mu$ is the dynamic viscosity of the fluid.

**Figure 4.15** Velocity field solved by FEM of flow through an irregular cross-section of a pore.

**Figure 4.16** Dimensionless hydraulic conductance versus shape factor for 100 pore cross-sections (throats) of a simulated cement paste, 100 random triangular and 100 random quadrilaterals cross-sections.
FEM at an adequate number of random cross-sections in the pore space. The obtained values are then used to form a function to obtain the conductance for an arbitrary pore throat via its shape factor as input. For example, the conductance versus shape factor of pore throats of a hydrated cement paste is shown (under relative values to circular cross-section) and fitted by a one-parameter linear function as in Figure 4.17. In summary, the hydraulic conductance of a pore throat is given by

\[ C_{po} = C_{cir} \xi \] (4.44)

where \( \xi \) is the function accounting for the shape factor with the input of the ratio between the shape factor of the pore and that of the circle, as shown by Figure 4.17. The mean values of shape factor (under relative value to \( Sh_{cir} \approx 0.08 \)) and the slopes of the regression lines for the triangles, quadrilaterals and cement paste’s throats are respectively given in Table 4.2. It can be seen that the mean shape factor of the cement paste’s throats is smaller than those of the triangles and quadrilaterals. It can be concluded based on the slopes of regression lines that the throat of cement paste at the same value of shape factor has a larger conductance than those of triangles and quadrilaterals.

### Table 4.2 Mean shape factors and regression parameters of different cross-section shapes

<table>
<thead>
<tr>
<th>Shape</th>
<th>Triangular</th>
<th>Quadrilateral</th>
<th>Throat of cement paste</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Sh_{mean}/Sh_{cir} )</td>
<td>0.49</td>
<td>0.61</td>
<td>0.31</td>
</tr>
<tr>
<td>( \tan(\xi) )</td>
<td>1.14</td>
<td>1.11</td>
<td>1.28</td>
</tr>
</tbody>
</table>


4.3.4 Examples

4.3.4.1 Simple cases

The generation, classification and main-trunk extraction of the virtual trees by DRaMuTS are validated through two simple cases. Two solid cubes with side length of 100 units contain hollow square-sectional tubes going (partly) through the specimens from bottom to top surfaces. The solid phase is constituted by densely overlapping spherical particles with a radius of 2.5 units placed at spacing of 2.5 units in all dimensions. The tubes inside the specimens are created by removing a number of spherical particles. The configuration of the tubes in the two specimens is schematized in Figure 4.18. Case I contains tubes with different sizes, whereby the throat size distribution of pores estimated by DRaMuTS can be validated. Case II contains different types of tubes reflecting the isolated pores and the main-path versus branching dead end pores of the percolated pore system.

The tree systems generated by the DRaMuTS are visualized in Figure 4.19, in which the trees exploring the percolated pores are distinguished. The extracted main trunks before and after smoothing from the tree systems are depicted in Figure 4.20. The throat size distribution is shown in Figure 4.21 for a comparison between the actual and the computed (by SVM) throat sizes. It is noticed that the walls of hollow tubes are not perfectly flat but roughly formed by the surfaces of the spherical particles, which causes the difference in throat size between SVM and actual assessment. The intrinsic permeability values of the specimens obtained by DRaMuTS are compared to those of analytical calculations, presented in Table 4.3. The difference in permeability values is again caused by the imperfect tube walls; the analytical values are estimated on the basis of perfectly square tubes. The conductance of an ideal square section of side length $a$ is given by

$$\text{size: 2.5, 5, 7.5, 10, 12.5}$$

Case I (horizontal section layout)  
Case II (vertical section layout)

Figure 4.18 Configuration of tubes in the specimens: Case I (top view of square tubes running from bottom top) and Case II (side view of square tubes).
\[ C_{\text{square}} = \frac{7a^4}{200\mu} \]  

(4.45)

Figure 4.19  Expansion of trees in tubes. The ‘blue’ colour denotes the trees exploring the percolated system

Figure 4.20  Extracted main trunks before (top) and after (bottom) smoothing.
Permeability estimation for a virtual porous medium

4.3.4.2 Virtual cement pastes

The DRaMuTS is applied to explore the flow paths and then the permeability of the representative cubes of the matured cement pastes described in Section 3.3.4 of Chapter 3. The pore features (i.e., porosity and ITZ thickness) of the specimens are shown in Table 3.2.

Figure 4.22 visualizes the virtual trees expanding in the pore space of the cement specimens. The main trunks extracted from the trees system are shown in Figure 4.23. The permeability values of cement specimens estimated by the tube model (Table 4.4) are shown to be in good agreement with those estimated by the FEM Stokes solver (Table 4.1).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Case I</th>
<th>Case II</th>
</tr>
</thead>
<tbody>
<tr>
<td>DRaMuTS</td>
<td>0.278</td>
<td>0.284</td>
</tr>
<tr>
<td>Analytical</td>
<td>0.228</td>
<td>0.315</td>
</tr>
</tbody>
</table>
4.4 Summary

Two methods to predict the permeability of porous materials are presented, using FEM and the so-called tube model to estimate the slow, stable and incompressible flow at pore-scale through virtual 3D representations of the porous materials.

<table>
<thead>
<tr>
<th>Coded name</th>
<th>W25F300</th>
<th>W40F300</th>
<th>W40F420</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coupled ITZ+bulk</td>
<td>1.446e-16</td>
<td>3.996e-15</td>
<td>1.600e-15</td>
</tr>
<tr>
<td>Bulk</td>
<td>7.522e-17</td>
<td>3.060e-15</td>
<td>1.270e-15</td>
</tr>
<tr>
<td>ITZ</td>
<td>3.643e-16</td>
<td>6.915e-15</td>
<td>3.102e-15</td>
</tr>
</tbody>
</table>

Table 4.4 Intrinsic permeability ($m^2$)
The first method, i.e., FEM Stokes solver, is applied to the voxel-based representation, in which each voxel is used to configure a cubic mixed (pressure-velocity) finite element to solve the Stokes equation. The velocity fields in virtual cement cubes solved by the FEM Stokes method demonstrate the gradient structures of flow velocity, whereupon the average velocity in the ITZ is shown to be larger than that in bulk zone. The FEM Stokes solver in this study, however, is used limitedly for voxel-based representation of materials. The FEM mesh is based on the lattice system of cubic finite elements of mono-sized, leading to high computational efforts for estimating the permeability of porous media with complex tortuous pore structures.

The second method, ‘tube model’, is based a network of hollow tubes representing the percolated pore system of a porous medium. The tube network is constructed by extracting the main trunks from a system of virtual trees growing fully in the percolated pores, based on a porosimetry named DRaMuTS. The extracted main trunks, having a zig-zag shape, are geometrical smoothed to get proper information of the flow paths through the material specimen. The equivalent diameters along the tubes are estimated by the enhanced SVM, measuring the local throat sizes around the tube axes. The irregular shapes of the pore cross-sections are taken into account in estimating the hydraulic conductance of the tubes. Compared to FEM Stokes solver, the tube model is computationally superior since it is developed particularly for the vector-based representation of the porous materials. Moreover, the isolated as well as branching dead-end pores are excluded in constructing the tube network, resulting in additional computational efficiency.

It can be seen that the permeability values of the simulated cement pastes predicted by the proposed methods agree well with those by the other methods that are specifically developed for the virtual cement pastes based on vector approach. In a research work carried out by Pignat et al. [107], for example, the intrinsic permeability of a simulated cement paste (w/c = 0.4) at the porosity of 19% is estimated approximately to be 3.4e-15 (m²), in which cement grains are also modelled by spherical particles.

Nonetheless, the permeability estimated on simulated cement pastes are about three orders of magnitudes different from those experimentally estimated on physical pastes. For example, the water permeability of PC pastes at a porosity of 19% estimated to be 2.8e-18 and 1e-18 (m²), respectively, by Odler and Köster [134] and by Banthia and Mindess [135]. The gap would come from two main reasons: the difference in microstructure between simulated pastes and physical pastes and the changes in microstructure of the cement pastes during the experimental procedures. XIPKM assumes the hydration products to be deposited on the particles’ surfaces as smooth and spherical layers. In reality, however, the hydration products precipitate as irregular layers surrounding the particles, leading to the more tortuous and blocked pore space than those in numerical cement pastes. The experimental procedure for estimating water permeability of cement pastes also influences the obtained results; the so-called ‘self-sealing effect’ (SSE) [18] causes a reduction of
the flow rate during experiment. This phenomenon is the consequence of changes in pore structure during the process due to several reasons:

- dissolution, deposition and crystallization of soluble phase (especially of CH) along the flow paths,
- continuing hydration by water saturation,
- flow path blocking by movement of loose particles under high pressure,
- swelling and shrinkage of the CSH gel due to re-saturation.

Indeed, in case a gas (i.e., oxygen) which does not react with any phase of hydrating cement paste (thus does not cause change in the microstructure) is selected as an intrusion fluid, the estimated permeability of a physical paste at a 19.3% porosity (i.e., 6.5e-17 (m²) by Wong et al. [131]) is one order of magnitude larger than above-mentioned water permeability.
Chapter 5 Investigation of pore characteristics and permeability of cementitious materials

Several tests are carried out on simulated cementitious materials by applying the computational schemes presented in the previous chapters. Aim is to evaluate the influence of different parameters on the pore characteristics as well as on permeability in a computationally efficient way. The investigations focus on the paste zone between two neighbouring aggregate surfaces, since this zone has the most significant impact on permeability as well as on fracture behaviour of concrete. The inhomogeneity of the pore structure in this zone is also discussed.

It is important to obtain a representative property of heterogeneous material. In other words, a representative volume element (RVE) for such a property should be demonstrated. There is not a unique definition of an RVE for heterogeneous materials [137-138]. In general, a sample of material is considered an RVE once (i) an increase in its size does not lead to significant difference in a property of interest of material and (ii) the sample is large enough so as to provide a reasonably accurate estimation of the property in a stochastic way. In this chapter, the existence of RVEs for various pore characteristics will be discussed.

It is well known that partial replacement of Portland cement (PC) by pozzolanic mineral admixtures can have direct positive effects on particle packing density (thus on compressive strength) and on transport-based durability. However, also the global CO$_2$ emissions are reduced by blending of the PC. Yet, the quantitative assessment of such technological profits constitutes a complicated and time-consuming problem particularly in experimental approaches. This chapter, therefore, also presents analyses, whereby PC is blended with incinerated rice husk ash (RHA), a vegetable waste. The investigations are carried out on several specimens of plain and blended cement pastes to evaluate the effect of RHA-blending on particle packing, pore characteristics and permeability.

*Parts of this chapter are submitted to Cement and Concrete Composites (Le and Stroeven [136])
5.1 Existence of RVE on the aspect of pore characteristics of cementitious materials

Cementitious materials belong to the category of particulate composites. The inherent heterogeneity on different structural levels is associated with scatter in data of the same descriptive parameter pertaining to a series of identical samples with either dimensions on meso- or micro-level [139]. The descriptive parameters can be global porosity, mean pore size, average Young’s modulus, tensile strength, etc. Changing linear dimensions of a sample would impact on the standard deviation of the global values of the selected parameters. Therefore, heterogeneity is not a material characteristic, but it is a function of the descriptor selected to describe certain aspects of material structure, and of the linear size ratio of the sample and the largest structural element [139]. Increasing the linear dimension of a sample will reduce the heterogeneity of an individual descriptive parameter to an acceptable low level (i.e., homogeneity), whereupon the representative volume element (RVE) is obtained for that particular parameter. In other words, the RVE is the minimum sample volume to represent materials on a particular aspect of material structure or material behaviour. Increasing this volume should not lead to a significant change of the relevant parameter. For more detailed definitions of the material heterogeneity and RVE, see [137,139-140].

Basicallly, a specific RVE size can be defined for each independent aspect of material structure or of material behaviour. The RVE is commonly characterised by the ratio between its size and the maximum structural parameter (e.g., grain size or pore size). Such a ratio should be large enough to approach a state of homogeneity but small enough to realize favourable computational conditions. Van Vilet [141] and van Vilet et al. [142] in their experiments on concrete’s tensile strength suggest the RVE size to be equal to 7-8 times the maximum aggregate size. Bažant and Oh [143] and Bažant and Pijaudier-Cabot [144] in their studies on the width of crack band proposed that the characteristic RVE size equals 2.7-3.0 times the maximum aggregate size. Stroeven et al. [145-146] suggest the RVE size to equal 4-5 times the maximum grain size for concrete’s density (being a composition parameter), but the RVE for a highly configuration-sensitive parameter can be significantly (up to one order of magnitude) larger. For more definitions of minimum RVE size, see [137].

The RVE existence for various pore characteristics is emphasized in this study. This is realized by considering the dependence of porosity, pore size distribution, porosity gradient and ITZ thickness on the sample size. This renders possible assessing the associated RVE size. The size dependence is investigated on cement specimens varying in size (80, 100, 120 and 130 µm), with w/c = 0.4 and a cement particle size range of 0.41-33 µm. The microstructural randomness of pore distributions is considered by four realizations for each sample size, so totally 16 samples are investigated. Each cubic specimen has four periodic and two opposite rigid boundaries to simulate the paste zones (including ITZ and bulk zones) between the aggregates’ surfaces. The simulation of the specimens in the fresh state and their evolution during hydration are implemented with the schemes presented in Chapter 2. The input parameters for simulating hydration by XIPKM are similar to those of...
specimen W40F300 described in Table 5.1 and Table 5.2 (see Section 5.3.1) but with different pocket sizes. The pore characteristics of the specimens are obtained by the scheme presented in Chapter 3. The pore size distribution functions are formed based on the smallest pore throats (Section 3.2.3).

The porosity evolution functions during hydration of the realizations at all sample sizes are in a good agreement as shown in Figure 5.1. It can be seen that the porosity evolution during hydration is independent from the sample size as well as the randomness of pore (particle) distribution in the range considered.

The porosity gradients (PoG) of the realizations for each sample size are depicted in Figure 5.2. The mean PoG function for each sample size is obtained by averaging the section porosity of four realizations at the corresponding location and is shown in Figure 5.3a. To eliminate the fluctuation, the original PoG functions of all realizations are firstly mathematically smoothed (see Section 3.3.2.3). The smoothed functions are then averaged to obtain a mean smoothed function of PoG for each sample size as shown Figure 5.3b. It can be seen that the mean smoothed PoG functions express the dependence on the sample size. However, only a slight size effect is shown since the difference between the sample size 80 µm and 130 µm is marginal. To quantify the stochastic deviation of porosity gradient between the realizations for each samples size, the following measure is introduced:

$$\sigma_{PoG} = \sqrt{\frac{1}{4 \times N} \sum_{i=1}^{N} \sum_{j}^{4} (\phi_{section,i}^{j} - \phi_{section,i}^{mean})^2}$$

(5.1)

where $N$ is the number of discrete sections along the direction normal to the rigid surfaces, $\phi_{section,i}^{j}$ is the sectional porosity at section $i$ of the smoothed PoG function of realization $j$ and $\phi_{section,i}^{mean}$ is that of the mean smoothed PoG for each sample size. The values of the deviation for the various samples sizes are plotted in Figure 5.4. The deviation of sectional porosity is shown to have a convergent tendency upon
increasing sample size. It converges at the sample size of 120 µm with a small value, i.e., 0.3% of the sectional area of a sample.

Figure 5.2  Porosity gradient of realizations for various sample sizes.

Figure 5.3  Mean porosity gradient functions for various sample sizes: (a) original function and (b) smoothed function.
The throat size distribution functions of the realizations for various sample sizes are shown in Figure 5.5. The mean functions of throat size distribution of four realizations for each sample size, obtained by averaging the volume fraction density at the corresponding throat size, are depicted in Figure 5.6. The throat size distribution is investigated separately for ITZ and bulk zone. It can be seen that the
throat size distribution in the bulk zone is shown to be insensitive to the sample size change in the range considered. On the other hand, the throat size distribution in the ITZ is shown to have a size effect in the sample size range 80~100 µm and reveals only size independence for the sample size exceeding 120 µm. The stochastic deviation analysis of throat size distribution between the realizations for each samples size is given by the following measure:

\[
\sigma_{ThSD} = \sqrt{\frac{1}{4N} \sum_{i=1}^{N} \sum_{j} \Delta s^2 \left( P(s_i)^j - P(s_i)^{mean} \right)^2}
\]  

(5.2)

where \(N\) is the number of discrete throat size \(s_i\) with interval \(\Delta s\) from minimum to maximum values of the measured throat sizes. \(P(s_i)^j\) is the corresponding value of the throat size distribution function of realization \(j\) and \(P(s_i)^{mean}\) is that of the mean throat size distribution function for each sample size. The statistical deviation of throat size distribution for each sample size is shown in Figure 5.7. The throat size distribution is shown to be insensitive to the microstructural randomness by the very small values of the deviation, \(i.e.,\) the fractions of \(1e^{-3}\) ~ \(3e^{-3}\) on the total pore volume. The deviation values are shown to be smaller for the bulk zone than for the ITZ.

It can be summarized that the global porosity is insensitive to the sample size as well as the microstructural randomness. The porosity gradient function is shown to be only slightly sensitive to the sample size effect and the stochastic microstructure observed by the marginal difference in the porosity gradient and small value of stochastic deviation for the range considered. The throat size distribution reveals the insensitivity to the randomness of microstructure. The throat size distribution obtained in the bulk zone is shown to be independent to the size effect, whereas the independence of throat size distribution in the ITZ is only revealed for the sample size exceeding 120 µm. Hence, it can be concluded in the present case where the maximum size of fresh cement particles is 30 µm that the size of the RVE can be 2.7 to 4.3 times the maximum grain size for the investigation of pore characteristics.

Figure 5.6  Mean throat size distribution for various sample sizes in: (a) ITZ and (b) bulk zone.
Investigation of pore characteristics and permeability of cementitious materials

This proposed size range is in good agreement with the practical average surface distance between two neighbouring aggregates in concrete which is found to be 70~100 µm [101].

5.2 Effect of rice husk ash blending

Portland cement production contributes worldwide by about 6% to CO₂-emissions, with inevitable effects on global warming. Growing building activities, particularly in South American and Southeast Asian countries, put extra pressure on concrete technology to come up with measures to reduce the amount of Portland cement per cube of concrete used for realization of infrastructural facilities and for high-rise building construction. Partial replacement of the Portland cement by pozzolanic mineral admixtures has been proven a possible option. The green character is even reinforced by making use of incinerated vegetable waste, such as rice husk ash (RHA). Furthermore, use of an admixture of vegetable origin such as RHA will additionally contribute to waste management and by its incineration energy to energy conservation.

The principle of gap-gradings the aggregate and the positive effects this can exert on aggregate packing and thus on concrete strength are known for a long time. More recently, this principle has been applied for the development of (super) high performance cementitious composites. As a consequence, particle packing has become a relevant issue in concrete technology. An illustration of simple gap-graded particle mixture in comparison with other types of grading is shown in Figure 5.8. The gap-gradings efficiency results from the small particles being effective fillers of the openings left by the large particles, which significantly reduce the spacing between the particles and thus improve the packing density.

Similar packing effects are also revealed on micro-level. Bui et al. [147] investigated the combination of fine-grained rice husk ash and Portland cements of different fineness. The mean particle size of RHA was around 5 µm, which is significantly smaller than that of normal PC cement of around 15~30 µm. The effect
of RHA blending on improving compressive strength has been demonstrated [99,147]. Major evidence is also coming from tests by Goldman and Bentur [100], whereby the blending material was inert. A direct observation of the blending efficiency on particle packing has been revealed in the computational study by Hu [13].

Investigating the effect of RHA-blending on pore structure as well as on transport-based properties of cementitious materials is not a simple task, especially by experimental methods. However, such investigation can be carried out in an economic way on simulated cementitious pastes, based on the procedures presented in Chapter 2–5.

5.3 Experiments

5.3.1 Input parameters

Various plain and pozzolanic-blended cement specimens are used to investigate the influence of different input parameters, i.e., \( w/b \) ratio, cement fineness, and blending dosage on the pore characteristics. The material properties of cement and pozzolanic admixture and the corresponding input parameters for simulating the microstructural evolution during hydration are described in Table 5.1 (see Chapter 2 for parameter notations). The reference pozzolanic admixture is a rice husk ash that was produced by incinerating a Vietnamese rice ash and ground during 18 hours, and is designated as ‘RHA\(_{18}\)’. Properties and production procedure are detailed in Bui [99]. As an example for the notation used for mixtures, ‘W40F300R20’ is the code of a blended specimen with \( w/c = 0.4 \), ‘cement fineness of 300 m\(^2\)/kg’ and ‘20% RHA blending’. The details are presented in Table 5.2. The specimens are simulated in a cubic container with two rigid walls, at the left and right sides, and four periodic ones to simulate the paste zones (including ITZ and bulk zones) between the aggregate surfaces.

The procedure for reducing the particle size range and the assessment of particle numbers of the model specimens are described in Section 2.2.1. The associated particle threshold size (Section 2.2.1.4), \( d_o^{\text{threshold}} \), of each virtual material is
calculated in such a way that the corresponding cumulative fraction $f_o^{threshold}$ is around 2% as in Table 5.1. The porosity gradient, pore size distribution and permeability are investigated by the porosimetry methodology presented in Chapter 3 and Chapter 4. For each specimen, in this chapter, the pore characteristics are investigated on the entire specimen’s volume to study the composite properties of the paste zone near the aggregates’ surfaces in concrete.

**Table 5.1 Material properties and their corresponding simulation input data**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Cement I</th>
<th>Cement II</th>
<th>Pozzolanic admixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Portland</td>
<td>Portland</td>
<td>RHA [99]</td>
</tr>
<tr>
<td>Fineness (m²/kg)</td>
<td>300</td>
<td>550</td>
<td>-</td>
</tr>
<tr>
<td>$f_o$</td>
<td>0.542:0.278:0.064:0.117</td>
<td>0.649:0.193:0.081:0.078</td>
<td>-</td>
</tr>
<tr>
<td>$C_S: C_S: C_3A: C_4AF$</td>
<td>-</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>$b, n$ - cement</td>
<td>0.023, 1.107</td>
<td>0.067, 1.03</td>
<td>0.12</td>
</tr>
<tr>
<td>Size range (µm)</td>
<td>0.41-33</td>
<td>0.21-33</td>
<td>0.01-17.7</td>
</tr>
<tr>
<td>$d_o^{threshold}$ (µm)</td>
<td>0.95</td>
<td>0.47</td>
<td>0.4</td>
</tr>
<tr>
<td>$f_o^{threshold}$</td>
<td>0.02</td>
<td>0.02</td>
<td>-</td>
</tr>
<tr>
<td>$d_o^{eq}$ (µm)</td>
<td>0.65</td>
<td>0.31</td>
<td>0.12</td>
</tr>
<tr>
<td>$K_o$, C_S: C_S:</td>
<td>0.0557; 0.0064;</td>
<td>0.0513; 0.0064;</td>
<td>-</td>
</tr>
<tr>
<td>$C_3A: C_4AF$ (µm/h)</td>
<td>0.0373; 0.0056</td>
<td>0.0373; 0.0056</td>
<td>-</td>
</tr>
<tr>
<td>$K_o$, RHA (µm/h)</td>
<td>-</td>
<td>-</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Model container size: 100x100x100 (µm).

**Table 5.2 Sample code notations**

<table>
<thead>
<tr>
<th>Code</th>
<th>w/c (w/b)</th>
<th>Code</th>
<th>Cement fineness</th>
<th>Code</th>
<th>RHA blending (by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W25</td>
<td>0.25</td>
<td>F300</td>
<td>300 m²/kg</td>
<td>R10</td>
<td>10%</td>
</tr>
<tr>
<td>W40</td>
<td>0.40</td>
<td>F420</td>
<td>420 m²/kg</td>
<td>R20</td>
<td>20%</td>
</tr>
<tr>
<td>W50</td>
<td>0.50</td>
<td></td>
<td></td>
<td>R30</td>
<td>30%</td>
</tr>
</tbody>
</table>

### 5.3.2 Porosity evolution with hydration time

The global porosity evolution of the plain and blended cement specimens are shown in Figure 5.9. It can be seen that blending has the most effect on reducing global porosity at an advanced state of hydration. This is most obvious at higher w/b ratio. The RHA-blending dosage is the percentage by weight of the replaced amount of cement. Since the specific density of RHA is smaller than that of cement, partial cement replacement leads to an increase in the total volume of the solid phases. This automatically causes a reduction in the capillary porosity of blended pastes with respect to the plain paste at equal w/b ratio even before hydration ($t = 0$).

Figure 5.10 depicts the porosity evolution of the blended pastes with various blending dosages. Only marginal differences in porosity between the blended pastes are shown.
5.3.3 Porosity gradient

The smoothed functions in Figure 5.11 represent the sectional porosity gradients of the specimens at 90 days of hydration. The sectional porosity represents the pore fraction in a thin slice parallel to the rigid wall at a given distance to the rigid wall (Section 3.3.2.3). From the gradient functions, the ITZ/bulk boundaries of the specimens can be obtained by the proposed procedure presented in Section 3.3.2.3. The ITZ thicknesses of the various specimens are listed in Table 5.3. The ITZ thickness is revealed to increase with a higher w/c for plain cement paste, however there is no clear influence of blending effect on the ITZ thickness.
Investigation of pore characteristics and permeability of cementitious materials

Table 5.3 ITZ thickness of the specimens at 90 days of hydration

<table>
<thead>
<tr>
<th>Cement specimen</th>
<th>Global porosity (%)</th>
<th>ITZ thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W25F300</td>
<td>8.1</td>
<td>10.4</td>
</tr>
<tr>
<td>W25F300R20</td>
<td>7.9</td>
<td>8.1</td>
</tr>
<tr>
<td>W40F300</td>
<td>18.6</td>
<td>14.65</td>
</tr>
<tr>
<td>W40F300R10</td>
<td>16.5</td>
<td>16.3</td>
</tr>
<tr>
<td>W40F300R20</td>
<td>15.3</td>
<td>15.9</td>
</tr>
<tr>
<td>W40F300R30</td>
<td>16.4</td>
<td>23.0</td>
</tr>
<tr>
<td>W50F300</td>
<td>26.7</td>
<td>16.0</td>
</tr>
<tr>
<td>W50F300R20</td>
<td>22.2</td>
<td>17.8</td>
</tr>
<tr>
<td>W40F420</td>
<td>16.5</td>
<td>18.0</td>
</tr>
<tr>
<td>W40F420R20</td>
<td>14.8</td>
<td>14.6</td>
</tr>
</tbody>
</table>

5.3.4 Pore size distribution

When focus is on the use of pore size characteristics in a transport-based model, it seems more reasonable configuring the pore size distribution (PoSD) based on the smallest pore throats as presented in (Section 3.2.3).

The evolution in the pore size distribution (PoSD) of the plain versus the blended specimens with w/b = 0.4 is presented in Figure 5.12. The blending efficiency is revealed by the shift of the PoSD function to the left (i.e., a reduction in pore sizes)
at an early stage of hydration. Furthermore, the PoSD of the plain specimen is modified significantly from 7 to 365 days of hydration.

Figure 5.13 depicts the blending effect in the PoSD of cement pastes with different w/b ratios at 90 days of hydration. The blending efficiency is demonstrated in all specimens, by the shift of the PoSD function to the left. From the above investigations, it can be concluded that blending significantly reduces the pore size in a specimen. In addition to that the global porosity is reduced as shown in Figure 5.9.

In order to observe the effect of RHA-blending on the particle structure, the PoSD functions of plain and blended specimens are compared at the same porosity in
Investigation of pore characteristics and permeability of cementitious materials

Figure 5.15 Pore size distribution of blended specimens with different replacement percentages at the same porosity ($\approx 18\%$).

Figure 5.14. It can be seen that a higher blending percentage results in a PoSD that shifts to the left for the same porosity.

Figure 5.14 shows the PoSD of plain and blended specimens of a cement with two different values of fineness at the same porosity. The higher cement fineness results in a significant reduction in pore sizes. This blending efficiency is not observed for the cement paste with the high cement fineness. This cement paste has a ‘well-graded’ particle structure (Figure 5.16) with very small particle spacing in the fresh state. Blending leads to an excess of finer particles that may cause a perturbation in the grading with a lower density [26,148].

Figure 5.16 Pore size distribution of blended specimens with different cement fineness at the same porosity ($\approx 18\%$).
5.3.5 Permeability

Figure 5.16 depicts the evolution in permeability during hydration of the plain and blended specimens with \( w/b = 0.4 \). The permeability in the plain paste declines gradually and significantly for a long period of time starting from early hydration. On the contrary, the efficiency of blending is revealed by a much lower permeability of the blended specimen at early hydration and it diminishes only marginally after 28 days of hydration.

Figure 5.17 shows the permeability of the plain and blended cement pastes with different \( w/b \) ratios. The blending effect on reducing permeability of the plain cement specimens is shown.

Figure 5.18 presents the influence of the blending percentage on the permeability. The different plain and blended specimens are investigated at the same porosity. A reduction in permeability is revealed at increasing blending dosage. However, the permeability of the blended paste does not change significantly from 20% to 30% dosage.

Figure 5.19 shows the permeability of the plain and blended cement pastes with different cement fineness. The blending effect, again, is not revealed for the cement paste with higher fineness. This is due to the aforementioned perturbation effect in particle packing.

![Graph showing permeability evolution](image)

*Figure 5.16 Evolution of permeability during hydration in 7, 28, 90 and 365 days of plain and blended specimens with \( w/b = 0.4 \).*
Investigation of pore characteristics and permeability of cementitious materials

Figure 5.17 Permeability of plain versus blended specimens with different w/b ratios at 90 days of hydrations.

Figure 5.18 Permeability of blended specimens with different replacement percentages at the same porosity (≈ 18%).
5.3.6 Discussion

Porosity distribution inhomogeneity

The porosity gradient in the ITZ can be considered as a representation of the inhomogeneity of the pore distribution in the direction normal to rigid surfaces. To compare the inhomogeneity of the specimens having different global porosities, the porosity gradient is presented normalized by the bulk porosity (i.e., the average porosity in the bulk zone). The examples of the normalized porosity gradient are shown in Figure 5.20. The examples reveal that the porosity gradient is increased during prolonged hydration and at reduced w/b ratio.

To quantify the porosity inhomogeneity, the following measure is introduced:

\[
\sigma_{PoG} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \left( \frac{\phi_{\text{section},i} - \phi_{\text{bulk}}}{\phi_{\text{bulk}}} \right)^2}
\]

(5.3)

where \(N\) is the number of discrete sections along the direction normal to the rigid surfaces, \(\phi_{\text{bulk}}\) is the porosity in the bulk zone and \(\phi_{\text{section},i}\) is the sectional porosity at section \(i\). Outcomes representing the porosity inhomogeneity of the different specimens are shown in Figure 5.21. Figure 5.21a confirms the earlier observation: inhomogeneity of a paste increases with decreasing porosity during hydration. Figure 5.21b shows that the inhomogeneity increases slightly with RHA-blending percentage. The (blended) cement pastes with high w/b ratio (0.4 and 0.5) result in increased inhomogeneity as shown in Figure 5.21c. Finally, Figure 5.21(d) demonstrates the (blended) paste with higher fineness to have a reduced inhomogeneity.

Figure 5.19  Permeability of plain versus blended specimens with different cement fineness at the same porosity (≈ 18%) and w/b = 0.4.
Investigation of pore characteristics and permeability of cementitious materials

Figure 5.20  Examples of normalized porosity gradients.

Figure 5.21  Deviations of sectional porosity from bulk porosity representing inhomogeneity of porosity distribution in direction normal to rigid surfaces of specimens.
Anisotropic pore size structure

The pore structure in the paste between two neighbouring aggregate grain surfaces is different from that of a bulk cement paste (no aggregates included). The pore space between these surfaces will have an anisotropic structure because the aggregate packing has a significant impact on the cement particle structure in the direction normal to the aggregate surfaces.

To estimate the anisotropy in pore size, the cross-sections of the local pores cut by the planes respectively parallel and normal to the rigid walls at random points are studied. The size distribution of the pore cross-sections are depicted in Figure 5.22, separately for the ITZ and the bulk zone. In the ITZ, the size range of pore cross-sections parallel to the rigid walls is wider than that perpendicular to the rigid walls. It can be concluded that the anisotropic structure of throat sizes occurring in the ITZ leads to anisotropy of the permeability as well. In the bulk zone, the throat structure is isotropic since the size distribution functions of the pore cross-sections normal and perpendicular to the rigid walls are similar.

![Figure 5.22 Size distribution of pore cross-sections perpendicular and parallel to the rigid walls of W40F300 at 90 days of hydration.](image)

Median distribution pore sizes

The pore sizes of the porous material generally vary in a range as represented by the pore size distribution (as shown in Fig. 5.20). To study the effect of pore size distribution on the porous material’s properties (e.g., permeability, compressive strength), the median value $d_{0.5}$ of the pore size distribution can be used [149-150]. The median distribution size $d_{0.5}$ is the pore size corresponding to 50% volume fraction of the cumulative pore size distribution.

Figure 5.23 depicts $d_{0.5}$ versus global porosity of the plain and blended specimen with $w/b = 0.4$ during the hydration period from 7 to 365 days. The efficiency of blending in reducing the pore size is also reflected by a significant difference in
median pore sizes between the plain and blended pastes at the same hydration duration and the same porosity.

**Random pore throats**

Figure 5.24 shows the PoSD functions of different specimens configured based on throat sizes with a different definition from the smallest area throat investigated in 5.3.4. The throat size through a probing point is estimated by a single plane that is *randomly oriented* and denoted as ‘random pore throats’. The PoSD functions based on the *random pore throats* (Figure 5.24a) are shown to have a wider range than those based on the *smallest pore throats* (Figure 5.24b) with peaks are shifted to the right side. To quantify the relation between the two types of PoSD functions, the ratio of median distribution pore size between the random pore throats and the smallest pore throats is investigated for each available specimen and shown in

**Figure 5.23** Median pore size versus porosity of plain and blended specimens with w/b = 0.4.

**Figure 5.24** Pore size distribution of plain versus blended specimens with different w/b ratios at 90 days of hydration, characterised based on the random pore throats and smallest pore throat.
Interestingly, these ratios of all specimens are shown to be similar. All ratios are larger than one since a random cross-section leads to a larger area than the smallest pore throat. The average value of the ratios equals 1.45. It is noticed that the estimation of random pore throat is 6-8 times faster in computing time than that of smallest pore throat.

The investigated permeability data of all plain and blended specimens with different w/b ratios (0.25, 0.4 and 0.5) and different cement fineness (F300 and F550) at different days of hydration (7-365 days) are collected and shown as a function of the median size of random pore throat $d_{0.5, \text{rand}}$ in Figure 5.26 (circular marker). Obviously, the computational data can be approximated by a quadratic polynomial on a semi-logarithmic scale. Regression analysis yields the following expression for the solid line in Figure 5.26:

$$K (m^2) = a \cdot d_{0.5, \text{rand}}^2$$
Investigation of pore characteristics and permeability of cementitious materials

\[ \log(K) = -0.04d_{0.5,\text{rand}}^2 + 0.884d_{0.5,\text{rand}} - 18.5 \ (K \text{ in } m^2, d_{0.5,\text{rand}} \text{ in } \mu m). \] (5.4)

Based on this function, the prediction of permeability can be simply obtained from the size distribution of random throats, or even its median value. However, it is noticed the application of this function is only valid for cement pastes with particle data and sample size described in Section 5.3.1.

Shape factor and conductance of random pore throats

The mean shape factors, \( Sh_{po}^{\text{mean}} \) (see Section 4.3.3.2), of random throats of the plain and blended cement pastes relative to the circular cross-section (\( Sh_{cir} = 0.08 \)) are shown in Figure 5.27. Figure 5.27a reveals that the mean shape factor (or circularity) of pore throats in cement paste is around 0.3 times the shape factor of the circular cross-section and slightly increases with hydration duration. There is not a clear tendency for variation of shape factor with w/b ratio as shown in Figure 5.27b. The mean shape factor is shown to have a slight reduction by the blending effect.

By a similar procedure as mentioned in Section 4.3.3.2, a function representing the cross-section conductance versus shape factor is obtained for each specimen by a statistical one-parameter linear regression analysis, based on the relative values (to the circular cross-section) of shape factor and conductance of various random throats. The regression parameters (i.e., the slope of \( \xi \)) of various plain and blended cement pastes are depicted in Figure 5.28. It can also be seen that such a parameter is insignificantly influenced by the hydration duration, w/b ratio as well as the blending effect. The average value of this parameter over the investigated specimen is around 1.3.

Figure 5.27  Mean shape factor of random pore throats of various specimens.
5.4 Summary

The existence of an RVE in cementitious pastes with respect to different aspects of pore characteristics has been demonstrated for a sample size range of 80~130 µm with a maximum size of fresh cement grain of 30 µm. The determination of the RVE is based on the independence of sample size and deviation analysis of stochastic microstructure for individual pore characteristics of interest. The global porosity has been shown to be insensitive to the sample size, whereas the porosity gradient and throat size distribution are only slightly sensitive to the size effect as well as the microstructural randomness. The considered sample size range is in good agreement with the average mean spacing between aggregate surfaces which is around 70~100 µm in practice.

The effect of the rice husk ash blending on reducing porosity, pore size distribution and thus on improving the durability of cementitious pastes has been demonstrated. Blending has a significant effect in the very early hydration stage. This property, however, is only revealed for pastes with normal cement fineness. Blending of pastes with high fineness (550 m²/kg) gives rise to slightly negative effects on the pore structure.

Based on the porosity gradient, the inhomogeneity of the porosity distribution is quantitatively evaluated. The reduction in porosity during hydration evolution causes the inhomogeneity of the pore distribution to increase.

The size distribution of projected pore throats perpendicular and parallel to aggregate grain surfaces in the ITZ has been shown to yield an anisotropic structure of pore cross-sections. The pore throats perpendicular to the aggregate grain surfaces are shown to be smaller than the ones parallel to the rigid surfaces.

Figure 5.28 Slope of linear function representing cross-section conductance versus shape factor of various specimens.

(a) W40F300
(b) at 90 days of hydration
The median distribution size of the pore throats has been revealed to be almost in a linear relation to the overall porosity. However, this relation is distinguished between plain and blended pastes, shown by two separate functions.

The median distribution size of random throats, which can be assessed with significantly reduced efforts, is demonstrated related to the logarithm of the permeability by a quadratic polynomial function. Such a function renders possible simply estimation of the permeability from the mean pore size. However, the simplified estimation is only applicable for the cement pastes with input parameters of particles and sample sizes as described for the investigated specimens.

The median shape factor of pore throats in cementitious materials has been shown to be around 0.3 times the shape factor of the circle. The slope of the regression linear function, representing the cross-section conductance versus shape factor of pore throats in cementitious materials, has been revealed to be around 1.3. This value is expected to be used as an overall parameter to modify the conductance of model tubes (Section 4.3.3), taking the irregularity of pore cross-sections into account.
Chapter 6  Micro-mechanical behaviour of cementitious materials*

Strength as well as mechanical behaviour of a porous material such as matured cement paste are significantly dependent on its pore structure. In this chapter, the effects of pore characteristics on elasticity moduli and on tensile damage behaviour of cementitious materials are discussed. The plain and blended PC specimens presented in Chapter 5 are successively investigated regarding the micro-mechanical properties and behaviour.

Matured cement paste is at micro-scale a composite material composed of individual phases with different properties. The macro properties of the material can be obtained by a homogenization technique. In this study, the macro elastic properties of the cementitious specimens are predicted by an analytical homogenization technique, based on the intrinsic elastic properties of individual phases in matured (pozzolanic-blended) cement pastes experimentally obtained by nano-indentation.

Predicting damage evolution of materials by FEM application to 3D representations of materials is extremely computationally demanding. This chapter presents a proposed scheme to characterize tensile damage behaviour of porous quasi-brittle materials by FEM. The FEM tensile test is carried out on a representative 2D specimen in which the pore structure of the corresponding 3D specimen is incorporated. A representative 2D specimen is furthermore split into two sub-parts for representing ITZ and bulk zone separately.

The stress-strain response for tensile damage behaviour by a standard averaging technique has shown to be dependent on the size of the representative volume. In this chapter, a simple technique is proposed to prevent this size effect, thereby capturing the existence of a microscopic representative volume element (RVE).

* Parts of this chapter were published elsewhere (Le et al. [151])
6.1 Methodology

6.1.1 Assessment of elastic moduli of matured cement pastes

The individual elastic properties (i.e., Young’s modulus and Poisson’s ratio) of different cement phases were experimentally obtained by different authors. These values used in this study are obtained from Bernard [57] and are listed in the Table 6.1. The homogenized bulk and shear moduli, \( k_{\text{hom}}^{\text{est}} \) and \( \mu_{\text{hom}}^{\text{est}} \), can be determined, using the ‘self-consistent’ upscaling scheme [152-153]:

\[
\begin{align*}
    k_{\text{hom}}^{\text{est}} &= \sum_r f_r k_r \left( 1 + \alpha_{\text{hom}}^{\text{est}} \left( \frac{k_r}{k_{\text{hom}}^{\text{est}}} - 1 \right) \right)^{-1} \\
    \mu_{\text{hom}}^{\text{est}} &= \sum_r f_r \mu_r \left( 1 + \beta_0^{\text{est}} \left( \frac{\mu_r}{\mu_{\text{hom}}^{\text{est}}} - 1 \right) \right)^{-1}
\end{align*}
\]

(6.1)

(6.2)

with

\[
\alpha_{\text{hom}}^{\text{est}} = \frac{3 k_{\text{hom}}^{\text{est}}}{3 k_{\text{hom}}^{\text{est}} + 4 \mu_{\text{hom}}^{\text{est}}} \quad \beta_0^{\text{est}} = \frac{6 \left( k_{\text{hom}}^{\text{est}} + 2 \mu_{\text{hom}}^{\text{est}} \right)}{5 \left( 3 k_{\text{hom}}^{\text{est}} + 4 \mu_{\text{hom}}^{\text{est}} \right)}
\]

(6.3)

where \( r \) stands for cement phases and \( f_r \) denotes the volume fraction of the phases. \( k_r \) and \( \mu_r \) denote the bulk and shear moduli of the cement phases. It can be seen that the equations (6.1) and (6.2) constitute a system of nonlinear equations with unknowns \( k_{\text{hom}}^{\text{est}} \) and \( \mu_{\text{hom}}^{\text{est}} \). These equations are solved iteratively to obtain the homogenized bulk and shear moduli. Finally, the homogenized Young’s modulus and Poisson’s ratio at macro scale are given by the elasticity formula [57]:

\[
\begin{align*}
    E_{\text{hom}}^{\text{est}} &= \frac{9 k_{\text{hom}}^{\text{est}} \mu_{\text{hom}}^{\text{est}}}{3 k_{\text{hom}}^{\text{est}} + \mu_{\text{hom}}^{\text{est}}} \quad \nu_{\text{hom}}^{\text{est}} = \frac{3 k_{\text{hom}}^{\text{est}} - 2 \mu_{\text{hom}}^{\text{est}}}{6 k_{\text{hom}}^{\text{est}} + 2 \mu_{\text{hom}}^{\text{est}}}
\end{align*}
\]

(6.4)

In this study, the 3D representations of (blended) cement pastes are simulated by XIPKM, whereby the fraction of each individual phase at each hydration time step can be obtained. Therefore, the elastic modulus at macro-level of the cementitious specimens can be obtained by the above-mentioned representative procedure. It is

<table>
<thead>
<tr>
<th>Table 6.1 Elastic moduli of cement phases [57].</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>( E ) (GPa)</td>
</tr>
<tr>
<td>( \nu ) (-)</td>
</tr>
</tbody>
</table>
noted that pore fraction is also included in such calculations with the assumption that pore is a phase with Young’s modulus $E_r = 0$ and Poisson’s ratio $v_r = 0$.

### 6.1.2 2D representative specimen for mechanical tests

#### 6.1.2.1 Porosity representation

For the investigation of the influence of pore structure on the damage behaviour, a cementitious paste is assumed in this study which contains only two phases, i.e., pore and solid. To avoid extremely computational demanding FEM analyses on a 3D specimen of the cementitious material, a 2D porous specimen is used for the mechanical tests, which incorporates a projected version of the 3D pore structure. The basic idea of this 2D representative specimen is that the topology of the 3D pore structure is projected onto a plane to obtain a porosity field. This porosity field expresses the variation in intensity of the projected pores on the plane and thus can be considered as a 2D representation of the 3D porous specimen in case of a plane stress condition.

The procedure to generate the 2D representative specimen starts with a uniform at random (UR) generation of points in the 3D pore space in the same way as presented in the RaNoS porosimetry (Section 3.3) (Figure 6.1a). The system of these UR points as a discretized representation of the 3D pore structure is then projected onto a plane (for example, on the x-z plane as can be seen in Figure 6.1b. The field expressing the density of pores projected onto the plane is reflected by the density variations of the projected points. Taking a small area $\Delta A$ of the plane at a location $(x, z)$, the corresponding pore density is calculated by

![Figure 6.1](image.png)
where \( n_p(\Delta A) \) and \( n_p(A) \) denote the numbers of projected points inside \( \Delta A \) and inside the whole area \( A \) of the projection of the 3D specimen, respectively. An example of the porosity field is depicted in Figure 6.2.

6.1.2.2 Material representation

Material damage model

The tensile test on a 2D representative specimen is investigated using FEM where the softening behaviour is characterised by a simple isotropic elasticity-based damage model described by the stress-strain relation

\[
\sigma = (1 - \omega) D : \varepsilon
\]

(6.6)

where the second order tensor \( D \) contains the elastic moduli and the scalar \( \omega \) describes the damage value. The damage evolution is taken according to the following exponential law

\[
\omega = \begin{cases} 
0 & \text{if } \kappa < \kappa_I \\
1 - \frac{\kappa}{\kappa_I} \left[ 1 - \alpha + \alpha e^{-\beta(\kappa - \kappa_I)} \right] & \text{if } \kappa \geq \kappa_I 
\end{cases}
\]

(6.7)

where \( \alpha \) (residual stress), \( \beta \) (softening slope) and \( \kappa_I \) (damage threshold) denote the inelastic parameters. The variable \( \kappa \) is the maximum strain ever reached in history given by the loading function:

\[
f = \vec{\varepsilon}_{eq} - \kappa \leq 0, \quad \kappa \geq 0, \quad f\kappa = 0
\]

(6.8)

in which \( \vec{\varepsilon}_{eq} \) is the nonlocal equivalent strain that is given by the ‘gradient enhanced damage model’ [154]:

Figure 6.2 Porosity field on 2D representative specimen.
Micro-mechanical behaviour of cementitious materials

\[ \bar{\varepsilon}_{eq} - c\nabla^2 \bar{\varepsilon}_{eq} = \varepsilon_{eq} \]  

(6.9)

where \( c \) is the gradient parameter. The equivalent strain is defined according to Mazars [155] for concrete given by

\[ \varepsilon_{eq} = \sqrt{\left(\varepsilon_1\right)^2 + \left(\varepsilon_2\right)^2 + \left(\varepsilon_3\right)^2} \]  

(6.10)

where \( \langle \varepsilon_i \rangle \) denotes the positive values of the principal strains. The details of the finite element formation is given in [154].

Meshing with porosity field

The porosity field as afore-mentioned varies for different locations on the 2D specimen. Hence, the representation of material properties should also vary and depend on the location. To capture the difference in material properties at different locations, the 2D specimen is meshed into an adequate number of small triangular FEM elements (Figure 6.3), for each of which the pore density is assumed to be constant. The pore density of element \( i \) is also calculated by Eq. (6.5) with \( \Delta A \) replaced by the area of the element, \( A_i^p \). It is assumed that, in this study, only the homogenized Young’s modulus of an element depends on its pore density; the other parameters (e.g., Poisson’s ratio, parameters regarding the damage evolution law) are the same for all elements. Young’s modulus of element \( i \), taking into account the pore density, is given by

\[ E_i^p = \bar{E}(1 - \Phi_i^p) \]  

(6.11)

where \( \bar{E} \) is the homogenized modulus of the material calculated by Eqs. (6.1)-(6.4) including only solid phases (excluding the pore fraction). \( \Phi_i^p \) is the pore density averaged over element \( i \).

Figure 6.3    Mesh system of 2D representative specimen.
6.1.3 Tensile test configuration

The tensile test is carried out by fixing the left edge, while displacing the right edge to stretch the sample. At the upper and lower boundaries, periodic boundary conditions are applied. The response of the sample is visualized by a homogenized stress-strain diagram, where homogenized stress and strain in tension direction are simply calculated by

\[
\bar{\sigma}_x = \frac{f_{x}^{R}}{h}, \quad \bar{\varepsilon}_x = \frac{\bar{u}_x^{R}}{l}
\]  

(6.12)

in which \(f_{x}^{R}\) is the sum of horizontal nodal internal forces along the right side of the sample, \(\bar{u}_x^{R}\) is the imposed displacement applied at the right edge, and \(h\) and \(l\) are the height and width of the sample, respectively. The 2D representative specimen denoted ‘integrated’, obtained from a simulated 3D specimen of cement paste with two opposite rigid walls, is used to characterise tensile damage behaviour for the combined ITZ-bulk region (Figure 6.4a) between two nearby concrete aggregate’s surfaces. Such a 2D representative specimen is further more split at the ITZ borders into two parts to test the tensile damage behaviour of the ITZ (Figure 6.4b) and the bulk region (Figure 6.4c).

It should be noted that, to adequately characterise the composite behaviour of the paste zone between two nearby aggregates’ surfaces, not only the bulk zone and ITZ but also the interfacial bonding strength between ITZ and the aggregate are necessarily taken into account. This bonding strength is however neglected in this thesis; the interfacial bonding is assumed to be perfect (i.e., no detachment) during the tension process.

![Figure 6.4 Different types of meshed specimens subjected to tensile tests.](image-url)
6.1.4 **Micro-macro transition**

The mechanical behaviour at micro-scale can be transmitted to macro constitutive laws by means of computational homogenization schemes. This transition requires the existence of a microscopic representative volume element (RVE); i.e., an increase in the sample size does not impose a change in the homogenised properties. It has been shown that an RVE does not exist for softening quasi-brittle materials [156-157] with the standard averaging technique as given by Eq. (6.12). The non-existence of an RVE of such a technique, in this study, is demonstrated by porous samples of various sizes visualized by Figure 6.5. The difference in tensile damage response of the porous samples by the standard averaging technique is depicted in Figure 6.6; the larger the sample the more brittle is the homogenized response. This is due to the fact that the mesh-objective fracture zone which is determined by the length scale parameter \( c \) does not scale with the sample size.

![Image 1](image1.png)

**Figure 6.5** Samples of various sizes. All samples have the same porosity of 10% and include circular pores, whose sizes vary according to the same pore size distribution. The materials parameters are given the following: \( E = 31.106 \) GPa, \( \nu = 0.259 \), \( \kappa_i = 2 \times 10^4 \), \( \alpha = 0.99, \beta = 200, c = 0.5 \).
In this study, a simple technique is proposed to capture RVE existence, based on a transformation of the homogenised stress-strain relation. Let us consider a macroscopic rectangular sample under tension in x-direction with a cohesive crack inserted in y-direction (Figure 6.7). The displacement at the right edge is composed of two components: the elastic deformation in the continuous domain and the separation at the crack, given by

\[ u_x^M = \varepsilon_{x,\text{elastic}}^M l^M + u_x^{\text{crack}} \]  

(6.13)

where \( \varepsilon_{x,\text{elastic}}^M \) is the elastic strain, \( u_x^{\text{crack}} \) is the crack opening and \( l^M \) is the side length of the sample in the tensile direction. From another point, let us consider a micro porous (composite) sample under tension in x-direction in the softening state in which damage spreads locally in a zone. The displacement of the right edge of the micro sample is assumed to consist of two components: one by an ‘assumed elastic deformation’ over the entire domain and the other by the contribution of damage.

Figure 6.6 Homogenized responses of porous samples of various sizes obtained by a standard averaging technique.

Figure 6.7 Elastic sample with cohesive crack under tension.
expressed by

\[
\bar{\varepsilon}_x^{\text{crack}} = \bar{\varepsilon}_x^{\text{elastic}} l^m + \bar{\varepsilon}_x^{\text{dam}}
\]  \hspace{1cm} (6.14)

where \( \bar{\varepsilon}_x^{\text{elastic}} \) is the ‘assumed elastic strain’, \( \bar{\varepsilon}_x^{\text{dam}} \) is the averaged displacement due to damage and \( l^m \) is the side length of the sample in the tensile direction. \( \bar{\varepsilon}_x^{\text{elastic}} \) is determined by dividing the tensile force by the Young’s modulus. By relating Eq. (6.13) term by term to Eq. (6.14) \((l^M \approx l^m)\), \( \bar{\varepsilon}_x^{\text{dam}} \) can be considered as the crack opening at macro-level. From Eq. (6.14) the homogenized crack opening is given by

\[
\mu_x^{\text{M,crack}} = \bar{\varepsilon}_x^{\text{dam}} = \bar{\varepsilon}_x - \bar{\varepsilon}_x^{\text{elastic}} l^m = (\bar{\varepsilon}_x - \bar{\varepsilon}_x^{\text{elastic}}) l^m
\]  \hspace{1cm} (6.15)

where \( \bar{\varepsilon}_x \) is the homogenized strain obtained by the standard averaging technique given in Eq. (6.12). With the proposed homogenization technique, the existence of RVE for softening of the porous material is demonstrated in Figure 6.8. The traction-separation relationship extracted from the RVE is no longer dependent on the RVE size.

### 6.2 Existence of RVE in tensile damage response of cementitious materials

To demonstrate the independence of sample size on the tensile damage response of hydrated cement pastes, four cubic specimens with side lengths of 80, 100, 120 and 150 µm, respectively, with six periodic boundaries (to represent infinite bulk pastes) are used. All cement pastes have \( w/c = 0.4 \). The simulation of the specimens at the fresh state and their evolution during hydration are implemented with the schemes presented in Chapter 2. The pore structures of 3D cubes at 90 days of hydration are projected onto 2D to obtained representative 2D samples for tensile tests (Sections 6.1.2). The 2D samples are then meshed with the FEM triangular elements and are finally subjected to tensile tests configured in Section 6.1.3.
The materials parameters are given as follows: $E = 35.418$ GPa, $\nu = 0.262$, $\kappa_1 = 2 \times 10^{-4}$, $\alpha = 0.99$, $\beta = 200$, $c = 0.5$. It is noticed that the Young’s modulus and Poisson’s ratio are obtained by homogenising different solid phases in the hydrated specimens as aforementioned. The tensile damage responses of the samples are finally obtained by the proposed homogenization technique (Section 6.1.4).

The damage patterns of the samples are shown in Figure 6.9, whereas the tensile damage responses by means of the traction-separation relation are plotted in Figure 6.10. Although the significantly damaged zones (red zones) of the samples differ in shape and location between the specimens, the plotted responses of the samples are very similar. This demonstrates the existence of an RVE for the porous cementitious materials at micro-level.

![Damage patterns of 2D representative samples of cement pastes under uniaxial tension at the average strain of $4 \times 10^{-4}$.](image)
6.3 Parameter study results

6.3.1 Young’s modulus

In this section, the Young’s modulus ($E$) of the plain and rice husk ash (RHA)-blended cement specimens described in Chapter 5 are investigated. The influence of various parameters on $E$ will be discussed. The Young’s modulus pertaining to the (blended) cement specimens are calculated by the analytical homogenization scheme presented in Section 6.1.1. The pore fraction is also considered as a phase with $E = 0$ and $\nu = 0$ among different phases constituting the matured cement pastes at micro-level. The notations of the cement specimen’s parameters are given in Chapter 5 (see Table 5.2).

Figure 6.11 shows the homogenised values of Young’s and shear moduli of cement pastes at different w/c ratios in comparison with experimental results carried out by Haecker et al. [61]. The computational and experimental results at each w/c ratio are compared at the same degree of hydration. The figures show a good agreement between computed and experimental results, indicating the validity of the homogenization scheme for these parameters.
Figure 6.12 depicts the evolution in Young’s modulus of plain cement pastes during hydration for various water/cement (w/c) ratios, separately for the ITZ and the bulk zone. Figure 6.12a shows significantly smaller Young’s moduli for the ITZ than those for the bulk zone. The ratios of Young’s modulus between the bulk zone and the ITZ of the pastes at 90 days (2.1x10³ hours) of hydration are 1.31, 1.49 and 1.59 for w/c ratios of 0.25, 0.4 and 0.5, respectively. It can be inferred from this ratio that the relative difference in Young’s modulus between the bulk zone and the ITZ increases for increasing w/c ratio. Figure 6.12b shows the values of Young’s modulus versus porosity during hydration evolution. The cement pastes with various w/c ratios are shown to have slightly different Young’s modulus values at the same porosity; a lower w/c ratio leads to a higher Young’s modulus value for both ITZ and bulk zone. This can be explained by the fact that the fractions of unhydrated mineral compounds of Portland cement, which are the hardest parts of the matured cement phases, are larger for the paste with lower w/c ratio.
Figure 6.13 Evolution of Young’s modulus of cement pastes blended for various dosages of RHA (a) during hydration and (b) with porosity.

Figure 6.13 expresses the evolution of Young’s modulus of cement pastes for different blending dosages of RHA. Figure 6.13a demonstrates the insignificant impact of blending percentage on Young’s modulus. Figure 6.13b shows that at the same porosity, Young’s moduli of the blended pastes are also marginally different from those of the plain paste for both ITZ and bulk zones.

Young’s moduli of blended pastes are compared to those of plain pastes at different water/binder (w/b) ratios in Figure 6.14. Blending is more effective in increasing the Young’s modulus at larger w/b ratios; the difference in Young’s modulus between a blended paste and a plain paste is positive for w/c = 0.5 but negative for w/c = 0.25 as shown in Figure 6.14a. This efficiency is also visible in the plot of Young’s modulus versus porosity in Figure 6.14b. Overall, the blending does not have significant impact on the Young’s modulus.

Figure 6.14 Evolution of Young’s modulus of plain and RHA-blended cement pastes (bulk zone) for various w/b ratios (a) during hydration and (b) with porosity.
Figure 6.15 demonstrates the significant increase in Young’s modulus for a Portland cement with higher fineness. The difference in Young’s modulus between the plain and blended pastes of the same fineness is insignificant during hydration (Figure 6.15a), but for the same porosity (Figure 6.15b), Young’s moduli of blended pastes are shown to be slightly lower than those of plain pastes of the same fineness.

6.3.2 Tensile damage response

In this section, the damage responses under tension of the plain and RHA-blended cement specimens described in Chapter 5 are investigated; the influence of different parameters on the damage responses will be discussed. The pore structures of the 3D specimens are projected on 2D to obtain different types of 2D samples (i.e., ‘integrated’, ‘bulk’ and ‘ITZ’) as illustrated in Figure 6.4. It is noticed that the interfacial bonding between aggregate grains and cement paste is neglected in this study. The tensile tests are carried out on the ‘integrated ITZ-bulk’ samples to obtain the combined response of the paste region between neighbouring aggregate grains in concrete. The tensile tests are also performed separately on the ‘ITZ’ samples and ‘bulk’ samples to obtain the separate responses of these zones. Based on the proposed homogenization technique (Section 6.1.4), eventually, the tensile damage responses of the samples are investigated.

The notations of the cement specimen’s parameters are given in Chapter 5 (see Table 5.2). All ‘integrated ITZ-bulk’ samples have size 100x100 µm. The width of the ‘ITZ’ and ‘bulk’ samples are given in Table 6.2. The material model parameters are as followings: $\kappa_i = 2e-4$, $\alpha = 0.99$, $\beta = 200$, $c = 1.0$. Since this study focuses on the impact of the pore features on the damage response of matured cementitious materials, the difference in elastic property between various solid phases is neglected. The same Young’s modulus and Poisson’s ratio obtained by homogenizing the different solid phases as presented in Section 6.1.1 are used. The homogenized Young’s moduli for solid phases of the samples are given in Table 6.2.
Table 6.2 2D Sample widths and Young moduli of cement specimens at 90 days of hydration

<table>
<thead>
<tr>
<th>Cement specimen</th>
<th>Global porosity (%)</th>
<th>Bulk width (µm)</th>
<th>ITZ width (µm)</th>
<th>Homogenised Young modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W25PcCe300</td>
<td>8.1</td>
<td>79.3</td>
<td>10.35</td>
<td>42.578</td>
</tr>
<tr>
<td>W25Po20Ce300</td>
<td>7.9</td>
<td>83.9</td>
<td>8.05</td>
<td>40.641</td>
</tr>
<tr>
<td>W40PcCe300</td>
<td>18.6</td>
<td>70.9</td>
<td>14.55</td>
<td>35.417</td>
</tr>
<tr>
<td>W40Po10Ce300</td>
<td>16.5</td>
<td>67.5</td>
<td>16.25</td>
<td>33.457</td>
</tr>
<tr>
<td>W40Po20Ce300</td>
<td>15.3</td>
<td>68.3</td>
<td>15.85</td>
<td>32.197</td>
</tr>
<tr>
<td>W40Po30Ce300</td>
<td>16.4</td>
<td>54.1</td>
<td>22.95</td>
<td>32.538</td>
</tr>
<tr>
<td>W50PcCe300</td>
<td>26.7</td>
<td>68.1</td>
<td>15.95</td>
<td>34.125</td>
</tr>
<tr>
<td>W50Po20Ce300</td>
<td>22.2</td>
<td>64.5</td>
<td>17.75</td>
<td>30.445</td>
</tr>
<tr>
<td>W40PcCe420</td>
<td>16.5</td>
<td>64.1</td>
<td>17.95</td>
<td>34.122</td>
</tr>
<tr>
<td>W40Po20Ce420</td>
<td>14.8</td>
<td>70.9</td>
<td>14.55</td>
<td>31.611</td>
</tr>
</tbody>
</table>
Figure 6.16 shows the examples of porosity fields of the 2D representative samples of cement pastes. The damage patterns of such samples at a highly damage state under uniaxial tension are visualized in Figure 6.17.

*Figure 6.16  Examples of porosity field of 2D samples representing plain and blended cement pastes at 90 days of hydration.*
Figure 6.17 Examples of damage patterns of 2D samples at 90 days of hydration under tension with average strain of $4 \times 10^{-4}$. There are three kinds of samples, i.e., ‘integrated’, ‘bulk’ and ‘ITZ’.
Figure 6.18 Comparison in tensile strength of between computational cement paste and experimental cement mortal [3].

Figure 6.18 depicts the tensile strength as a function of porosity of simulated specimens in comparison with that of cement mortal specimens experimentally carried out by Chen et al. [3]. The function for simulated pastes is obtained by collecting the maximum tensile stress and porosity of the ‘integrated’ specimens W25PcCe300, W40PcCe300 and W50PcCe300 (see Figure 6.21a and Table 6.2). The deviation between the computational and experimental results is expected since the simulated results are obtained from the representative specimens of cement paste (including the ITZ). The experimental results, on the other hand, are obtained from the cement mortal samples that are a complex system of sands and hydrating cement grains as well as ITZs between them.

Figure 6.19 indicates the responses of cement pastes with various w/c ratios. The tensile strengths of the integrated samples are obviously lower than those of the corresponding bulk samples and larger than those of the ITZ ones. The bulk samples are more ductile than the ITZ ones, as reflected by the smaller descending slopes the traction-separation relations. The bulk sample is more brittle with a lower w/c ratio. The responses of the integrated samples are shown to be more influenced by the

Figure 6.19 Tensile damage responses of samples representing plain cement pastes with various w/c ratios at 90 days of hydration.
ITZ, since they are noticeably similar to those of ITZ samples (regardless of the strength).

Figure 6.20 presents the responses in case of RHA-blended cement pastes. It can be seen that, although the global porosity of blended pastes is smaller than the plain one, blending results in a reduction in tensile strength. The higher blending dosage leads to a lower tensile strength. This can be explained by the decrease in the homogenized modulus of the blended pastes (Table 6.2). Figure 6.20b shows that higher blending dosages lead to a more brittle response of the bulk sample.

Figure 6.21 presents the influence of RHA blending at different w/b ratios. The higher w/b ratio (lower strength) results in the larger difference in tensile strength between the plain and the blended pastes. The more brittle behaviour of the blended ‘bulk samples’ can be explained by the pore structures observed in Figure 6.16; the pores are more localized at the region close to the ITZ-bulk boundary, and therefore the damage band zone is more localized as shown in Figure 6.17.

Figure 6.20  Tensile damage responses of samples representing plain and cement pastes (w/b = 0.4) blended with various blending dosages of RHA at 90 days of hydration. ‘p’ denotes the global porosity of a specimen.

Figure 6.21  Tensile damage responses of samples representing plain versus RHA-blended cement pastes with various w/b ratios at 90 days of hydration.
Figure 6.22  Tensile damage responses of samples representing plain and RHA-blended cement pastes (w/b = 0.4) with different cement fineness values at 90 days of hydration.

Figure 6.23  Normalized tensile damage responses of bulk samples.

Figure 6.22 depicts the responses of the cement specimens with different fineness values (i.e., 300 and 420 kg/m²). The reduction in tensile strength by blending occurs for both types of cement fineness. The responses in the bulk samples of the higher fineness are shown to be more brittle than the ones of the lower fineness. This phenomenon can be explained by the finer pore sizes in the specimens with the higher fineness. Finer pore sizes lead to a more brittle response of the bulk sample. This phenomenon is also revealed in Figure 6.19b, where blending results in finer pore sizes.

The tensile damage responses of the bulk zones in plain and blended specimens at different w/b ratios as shown in Figure 6.21b are normalized by the maximum traction and depicted in Figure 6.23. It can be seen that the normalized responses of the plain specimens coincide, whereas the normalized responses of the blended specimens are more brittle than the plain ones. Also, the normalized responses of the blended specimens are shown to be more brittle with lower w/b ratio.
6.4 Summary

A new computational scheme to predict the elastic moduli as well as the tensile damage response of matured cementitious materials is proposed in this chapter. The elastic moduli are predicted by an analytical homogenization method, based on the elastic properties of cement’s individual phases obtained experimentally in literature. To predict the tensile damage response, planar samples are created by projecting the 3D pore space onto a 2D plane. This avoids the use of extremely demanding 3D FEM representations of the material. The whole pore structure is taken into account on the 2D sample, which is an advantage over the 2D sample that is a cross section of the 3D specimen since a cross section or a number of cross sections is not sufficient to characterise the mechanical behaviour of the whole 3D specimen. The different behaviour in tensile damage response of the ITZ and bulk can also obtained, separating the sample at the ITZ boundary.

A simple technique is proposed to transform the stress-strain relation obtained by the standard homogenization technique into a traction-opening relation, whereby the existence of an RVE is guaranteed for a general porous material as well as the porous cementitious material. The proposed technique is also a basis to compare the tensile damage responses of the samples with different sizes.

Although the RHA-blending results in the effectiveness in the pore characteristics relating to the transport-based durability as presented in Chapter 5, the blending causes a reduction in Young’s modulus as well as tensile strength. The response of the ‘integrated’ samples combining the ITZ and bulk regions that represent the practical region between concrete’ aggregates has shown to be more influenced by the response of the separated ITZ sample. The finer average size of the pores in the bulk zone results in the more brittle tensile damage responses.
Chapter 7  Conclusions and recommendations

7.1 Conclusion

The continued progress in computer technology renders it possible nowadays to employ virtual materials as a more economic and still reliable option – as compared to conventional approaches. With novel computer technology material properties can be studied and behaviour of materials with a complex microstructure can be predicted. Therefore, a comprehensive methodological framework has been developed to exploit these capabilities for studying cementitious composites. It encompasses

- a novel method for generating virtual representations of cementitious composites at micro-scale;
- new porosimetry techniques for characterizing the pore structure of those virtual materials at any hydration stage;
- an economic micro-scale model for estimating permeability;
- an effective scheme for studying their tensile-damage characteristics.

The pore characteristics of hydrated cementitious composites have been studied by this newly developed methodology. The relations between different pore characteristics on transport and mechanical properties have been discussed.

It is well-known that experimental approaches for studying properties and predicting behaviour of materials are time-consuming, laborious and expensive. Difficulties derive from the specimen production, pre-treatment and costs of materials, instruments and labours, especially for materials with long-time microstructural evolution such as cementitious composites. Despite the complex and expensive process, physical methods do not always give direct results. Moreover, the material properties can also change during the experimental process. The general goal of this study, therefore, was to bring material studies into virtual reality as a cheaper alternative by developing the comprehensive method as summarized above.

The first contribution of this study is a novel computational model to simulate microstructural evolution of cement paste during hydration. The paste at the fresh
state is simulated by a dynamic packing process, employing an advanced DEM system (HADES). It has been found that this dynamic packing process renders it possible to generate a particle paste with very high density as well as a paste blended with particles of much finer sizes. This cannot be obtained by the random sequential addition (RSA) systems that are popular in particular structures in concrete technology.

The hydration model is based on a ‘vector approach’ that has major advantages over a ‘voxel approach’ due the latter’s voxel size limitations. The presented hydration model in this thesis - XIPKM - is an extension of the Integrated Particle Kinetics Model (IPKM), which was developed to simulate the evolution of a C₃S microstructure during hydration. The improvements of XIPKM as compared to other IPKM-based models include new conformations for particles as well as upgraded hydration kinetics for taking into account the four main compounds of a Portland cement (PC), a pozzolanic admixture and their chemical hydration products. The concept of ‘equivalent mono-sized fine particles’ is also a new development of XIPKM allowing the removal of a very large number of fine discrete particles from the designed mixture, however still accounting for the impact they have on the hydrating microstructure. This significant reduction in the number of particles has a positive effect on the computational time. These fine particles are commonly neglected in other vector-based models. In addition, the algorithms have been upgraded for controlling the complicated inter-particle contacts as well as the particle interferences during hydration – a crucial issue in vector approaches. Moreover, the hydration process of cement grains in XIPKM proceeds concurrently, thereby avoiding an order-based procedure common in other vector-based models.

The basic penetration rates, significant parameters of the model characterising the hydration process in vector-based hydration models, are generally estimated by a laborious calibration process. Such parameters are assessed in a much simpler way in this study. The basis is formed by a new numerical method, whereby the reaction rate parameters of different PC minerals are determined based on existing experimental data on hydrating cement pastes. Using this method, a good agreement in microstructural evolution was found compared to experimental data.

A new porosimetry technique denoted ‘Random Node Structuring’ (RaNoS) was successfully developed for virtual representations of porous material. It is demonstrated to be an economical and reliable approach. A prime advancement of such a method, as compared to physical methods, is the direct way pore characteristics can be derived from the 3D microstructure of the simulated material. For example, common physical experiments, such as MIP, provide pore size information that can be biased by orders of magnitude. Quantitative image analysis techniques only provide unbiased information on 3D pore size distribution for porous media having an isotropic pore structure. The method is also more straightforward than the serial sectioning and 3D reconstruction to the assessment of the pore microstructure. Pore exploration and delineation by RaNoS renders it possible to directly apply the ‘Star Volume Measure’ (SVM) to yield unbiased information on the 3D pore size distribution of the simulated microstructure. It is
noticed that the original SVM has been enhanced in this thesis for a more efficient size assessment of irregular-shaped pores. In addition, the determination of ITZ thickness inserted between the aggregate surface and the bulk zone of the cement matrix by an analytical method is another salient point of RaNoS. Finally, the ability to provide information on the degree of percolation of the pore structure is also seen as a significant advancement of RaNoS.

The core algorithm of RaNoS is based on a system of random points uniformly distributed in the pore space. As stated above, it allows for the assessment of various geometrical characteristics of the pore structure. For exploring the topology of the pore structure, RaNoS is enhanced with a system of concurrent virtual trees that grow randomly in pore space. The enhanced system is denoted ‘Double-Random Multiple Tree Structuring’ (DRaMuTS), which constitutes an important innovation in this study. DRaMuTS makes it possible exploring the highly tortuous and complex 3D pore topology of cementitious materials. The key algorithm of DRaMuTS originates from path planning techniques in robotics. In this study it has been enhanced to realize a higher efficiency.

The conversion of pore space into a cylindrical tube network system has been shown an efficient computational way for directly estimating the permeability at micro-scale. The tube network in this study is configured on the basis of the DRaMuTS tree system, which seems computationally superior as compared to the skeletonization techniques commonly used in other models. Furthermore, the impact of the non-circular shape of pores on the hydraulic conductance is also taken into account in this ‘tube model’. This approach has been validated by comparison with permeability obtained with a FEM Stokes solver.

Several tests were carried out on cement pastes blended with a silica-rich pozzolanic admixture, such as rice husk ash (RHA), by applying the presented methodologies. It was pursued to assess the influences exerted by different technological parameters on pore characteristics as well as on permeability. To do so, firstly, the size of the Representative Volume Element (RVE) was investigated for different pore characteristics pertaining to such cementitious materials. The size of such an RVE was shown to range from 2.7 to 4.3 times the maximum grain size, depending on the characteristics under investigation. The global porosity was shown structure-insensitive, while the porosity gradient and pore size distribution in the bulk zone were only slightly sensitive to the size effect as well as the microstructural randomness. The porosity gradient and pore size distribution in the ITZ were shown as the most sensitive to the size effect with RVE size around 4.0~4.3 times the maximum grain size.

Next, the effect of RHA-blending was investigated. RHA-blending reduces porosity, and the median pore size, thus potentially improving the durability of cement pastes. The blending efficiency was highest at early ages. The blending effect, however, is only significant for RHA finer than PC. Generally speaking, the effect depends on the differences between median particle sizes of RHA and of PC.
A final discussion focused on issues such as inhomogeneity and anisotropy in porosity. Furthermore, relations between the pore structural features were investigated. It was found that the inhomogeneity of the pore distribution increased at reduced overall porosity. The sizes of pore cross-sections have been shown anisotropic in the ITZ and isotropic in the bulk zone. The median distribution size of the pore throats declines linearly with the reduction of the global porosity, which is visualized by the distinct functions for plain and blended pastes. The median distribution size of ‘random throats’, which can be assessed with significantly reduced efforts, is revealed to be related to the logarithm of the permeability by a quadratic polynomial function. Therefore, it renders it possible to simply estimate the permeability from the mean pore size. The mean shape factor of pore throats in cementitious materials is around 0.3 times that of the circle. Additionally, the slope of the linear function representing the hydraulic conductance versus shape factor of pore throats in cementitious materials is around 1.3.

A new computational scheme to investigate elastic stiffness moduli as well as the tensile damage response of matured cementitious materials is presented in this dissertation. The tensile damage behaviour was studied based on representative planar samples created by projecting the 3D pore space onto a 2D plane. The advantage of this method over the common ones, such as 3D FEM models or (single) serial sectioning FEM models, is the dismissal of extremely demanding 3D FEM modelling. Nevertheless, it takes into account the impact of the complete 3D pore space. The different response of ITZ and bulk zone revealed by the proposed scheme is also a new element in concrete studies. A simple technique is proposed to transform a standard stress-strain curve into a traction-opening relation, whereby the existence of an RVE is guaranteed for the porous cementitious material. Blending effects exerted on the mechanical properties and on the behaviour of cementitious materials are also discussed. Although RHA-blending improves transport-based durability capabilities, it causes a reduction in Young’s modulus as well as in tensile strength. The global response of the paste zone between aggregate surfaces has been demonstrated to be disproportionately influenced by the ITZ. The smaller median pore size of the bulk zone resulted in a more brittle tensile damage response.

7.2 Recommendations

A comprehensive framework for simulating microstructural evolution due to hydration, able to explore pore characteristics and predicting behaviour of cementitious materials has been developed. Herein, it is shown to be an economic and efficient methodology for studying the material as well as mixture design. However, many unsolved issues are remaining for future research.

The cement grains are modelled as spherical particles in this study. However, it was stated by He [26] in a study on shape analysis of cement grains that the octahedron would be more appropriate for describing cement particles. This forms a challenge for simulating particle packing as well as microstructural evolution during hydration of cementitious materials. A more efficient way for detecting the complicated
interferences between non-spherical particles is required. As a consequence, also significant improvements of RaNoS as well as DRaMuTS have to be accomplished.

The permeability estimated on the simulated cement pastes in this study are orders of magnitudes away from those obtained in physical experiments that are mostly accomplished by MIP. It has been explained in Chapter 4 that part of the differences are due to well-known biasedness of MIP outcomes. Additionally, the hydration products in the vector-based approach used herein are deposited on the hydrating particles as smooth layers. This differs significantly from the irregular precipitation or crystallization of hydration products as observed in reality. The result is a reduction in pore sizes as compared to the presented simulated pastes. The irregular precipitation of hydration products can be described by adding fine particles, however on the expense of extreme computational efforts. Therefore, a multi-scale scheme is suggested in order to refine the distribution of hydration products on a lower scale (nano-level). The pore space between hydrating particles should be replaced by a porous medium that is modelled in an RVE containing solid particles and pores at nano-level. Consequently, the pore characteristics and permeability should be explored at the lower scale and eventually up-scaled to obtain the pore features at micro-level.

The tree system by DRaMuTS grows in the pores and gradually occupies the whole percolated network. The growth rate of the trees will definitely have a direct relation to the geometrical features as well as to the topology of the pore structure, and therefore, to permeability. Hence, parameters that characterise the growth rate of the tree system should be developed.

A scheme has been proposed in this study for predicting the damage process in cementitious materials that accounts for the impact of the 3D pore structure. This scheme makes use of a 2D condensed model to reduce computation efforts. However, developing an efficient way for simulating fracture process characteristics directly on a 3D model of the material would be of extreme interest. Since the virtual representation of materials in this study leads to a particle-based microstructure, it would be reasonable using DEM to simulate the damage response. Many 3D DEM models [158-160] have been studied for simulating the fracture process of brittle materials. However developing a DEM model for overlapping particles (e.g., by expansion during hydration) is still a challenge.
References


References


References


References


References


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Le Luong Bao Nhi
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List of relevant publication

Article - letter to the editor


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