Shaping Macroporous Ceramics
- templated synthesis, X-ray tomography and permeability

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Cover:
The cover shows simulated flow fields of fluid in the pore space of a macroporous alumina material. The solid material is not visible in this picture. The dark red colour represents high flow velocities and the light blue represents low flow velocities.

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Till mamma och till pappa. ♥
Tack.
Abstract

Macroporous ceramic materials have found widespread technological application ranging from particulate filters in diesel engines, tissue engineering scaffolds, and as support materials in carbon capture processes. This thesis demonstrates how the pore space of macroporous alumina can be manipulated, analysed in three-dimensions (3D) using visualisation techniques, and functionalised with a CO₂-adsorbing material.

A novel method was developed to produce macroporous alumina materials: by combining sacrificial templating with thermally expandable polymeric microspheres and gel-casting of an alumina suspension. This method offers a versatile production of macroporous ceramics in which the level of porosity and the pore size distribution can easily be altered by varying the amount and type of spheres. The permeability to fluid flow could be regulated by controlling the connectivity of the pore space and the size of the smallest constrictions between the pores. Sacrificial templating with particle-coated expandable spheres significantly increased the fraction of isolated pore clusters and reduced both the sizes and the numbers of connections between neighbouring pores, compared to templating with un-coated spheres.

The macroporous alumina materials were characterised with X-ray micro-computed tomography (µ-CT). The 3D data-sets obtained by X-ray µ-CT were used to calculate the spatial variation in porosity, the throat and pore size distributions and to calculate the permeability to fluid flow. The throat and pore size distributions were also able to be accurately quantified in only one extrusion and intrusion cycle with water-based porosimetry; a relatively novel and simple characterisation technique. The pore walls of the macroporous alumina materials were also coated with zeolite films by a colloidal processing technique. The CO₂-uptake of the coated alumina materials and of hierarchically porous monoliths of zeolites was evaluated and compared.

Key words: Alumina, ceramic, CO₂ capture, colloidal processing, expandable microspheres, gel casting, layer-by-layer, macroporosity, near-net shape, non-destructive evaluation, permeability, porosity, sacrificial templating, X-ray computed tomography
List of publications

This thesis is based on the following papers:


In this study I prepared the macroporous alumina materials and did the majority of the X-ray μ-CT data image analysis, as well as the major part of the data analysis and writing.


In this article I prepared the macroporous alumina material and performed the majority of the X-ray μ-CT data image analysis. I formulated the main outline of the article and did the majority of the data analysis and writing.


In this article I devised a method and produced the macroporous alumina materials with the expandable microspheres, I did all of the characterisation except for the mercury porosimetry, and did most of the data evaluation and writing.


In this study I devised a method to vary the permeability and produced the macroporous alumina materials, performed the majority of the X-ray μ-CT data image analysis, and did the major part of the data analysis and writing.
V. Linnéa Andersson, Farid Akhtar, Arto Ojuva, Lennart Bergström, *Colloidal processing and CO$_2$-capture performance of hierarchically porous Al$_2$O$_3$-zeolite 13X composites*. In manuscript.

In this study I formulated the process for preparing the materials, I did the characterisation with SEM and of the zeta potential, and the majority of the data analysis and writing.


In this article I formulated the method for applying the multi-layers of polyelectrolytes and colloidal particles onto the sacrificial templating material and assisted in the writing of the paper.

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# Table of Contents

Abstract

List of Publications

1. Introduction .................................................................................................................................1
   1.1 Porous ceramics ..................................................................................................................1
   1.2 Shaping macroporous ceramic materials .........................................................................1
   1.3 Structure and properties of macroporous ceramics .......................................................3
       1.3.1 The pore space and pore space accessibility .........................................................3
       1.3.2 The solid material and mechanical properties .....................................................4
   1.4 Application of porous ceramic materials in carbon capture ........................................4

2. Aims and objectives .....................................................................................................................6

3. Materials and methods .............................................................................................................7
   3.1 Materials and processing ....................................................................................................7
   3.2 Characterisation ..................................................................................................................9
       3.2.1 Scanning electron microscopy ............................................................................9
       3.2.2 Zeta potential ........................................................................................................9
       3.2.3 Differential scanning calorimetry ........................................................................9
       3.2.4 Thermo-gravimetry .............................................................................................9
       3.2.5 Thermo-mechanical analysis ............................................................................9
       3.2.6 Evaluation of porosity and density .......................................................................10
       3.2.7 CO₂-adsorption ..................................................................................................10
       3.2.8 Mercury porosimetry ........................................................................................10
       3.2.9 Water-based porosimetry ..................................................................................10
       3.2.10 X-ray micro-computed tomography ................................................................11
       3.2.11 Simulation of permeability .............................................................................11

4. Results and discussion .............................................................................................................13
   4.1 Three-dimensional visualisation and mapping of the macroporous space .........................13
       4.1.1 Introduction ............................................................................................................13
       4.1.2 Three-dimensional characterisation of macroporous materials with X-ray micro-computed tomography ........................................................................14
       4.1.3 Acquiring images with X-ray micro-computed tomography ................................14
       4.1.4 Image analysis and pore space identification of reconstructed X-ray tomogram data ........................................................................................................17
       4.1.5 Pore network identification and three-dimensional visualisation ...........................19
       4.1.6 Visualising the variation of porosity ......................................................................20
       4.1.7 Comparing X-ray micro-computed tomography with porosimetry methods ..........21
1. Introduction

1.1 Porous ceramics
The initial use of ceramics is reflected in the word itself originating from the Greek word “keramikos”, meaning fired clay. Pores have traditionally been avoided in ceramic products to increase the crack resistance, but in the last decades an increasing number of applications that require porous ceramics have emerged. Pores are commonly classified into three groups depending on their sizes: micro (<2 nm); meso (2-50 nm); and macro (>50 nm). Micro- and mesoporous ceramic materials are used as molecular sieves, in catalysis, and in controlled release applications, whereas the use of macroporous ceramics spans from traditional applications like roof tiles and concrete to advanced technical ceramics in medicine and automobile engines.

1.2 Shaping macroporous ceramic materials
There has been a significant development of various processing methods for the preparation of macroporous ceramics during the last 10 to 15 years. Partial sintering of powder compacts is the most straightforward route for producing macroporous bodies, however this method mostly yields low porosities (<60%) and few options to significantly alter the pore size distribution. Honeycombs with well-defined unidirectional channels can be paste extruded from a variety of ceramic powders and more complex three-dimensional macroporous ceramics can be produced by rapid-prototyping techniques, such as direct writing. Apart from these methods, it is possible to identify three different fabrication routes for producing highly porous macroporous ceramics: the replica, the sacrificial template and direct foaming methods (Fig. 3.1).

In the replica technique a perishable substrate, e.g. a polymer foam, is impregnated with a ceramic slurry, and excess slurry is removed to leave a thin ceramic coating on the surface of the polymer foam. After drying, the organic components must be removed at slow heating rates to allow for the gradual decomposition of the polymeric material and its diffusion through the ceramic coating before sintering. While this straightforward process is already established in industry to produce porous materials for e.g. molten...
metal filtration and diesel engine exhaust filters, there are limitations with respect to the mechanical stability of the final material and variability of pore sizes.\textsuperscript{21-23} After removal of the polymer foam, hollow cavities remain in the ceramic walls (struts) separating the pores,\textsuperscript{24,25} which significantly reduces the stress resistance of the final material. The method only yields open porosity, i.e. a connected pore space, and the smallest pore size achievable is limited to around 200 µm.\textsuperscript{12}

**Replica method**

![Diagram of the replica method]

**Sacrificial templating**

![Diagram of the sacrificial templating method]

**Direct foaming**

![Diagram of the direct foaming method]

Fig. 1.1 Scheme of three possible processing routes for making macroporous ceramic materials: the replica, the sacrificial template and the direct foaming methods.

In the sacrificial template method, a templating material is initially homogenously distributed in a continuous matrix of a ceramic phase and thereafter removed to result in a porous material. The dominating templating materials are organic materials, such as dense or hollow polymer beads,\textsuperscript{26-29} and freeze-dried liquids.\textsuperscript{30,31} The size, shape and arrangement of the
templating material offers significant versatility to independently tailor the porosity, pore size distribution and pore morphology. However, the removal of the organic templating material can be very time consuming and may also induce stresses and thus cause cracking and deformation of the material.  

The direct foaming technique relies on the use of surfactants or particles to stabilise a foam generated by mechanical frothing or bubbling of a gas through a suspension. To preserve the porous structure the foam needs to be consolidated by polymerisation, or by setting of proteins or polysaccharides. This technique allows for facile production of highly porous ceramic materials with dense pore walls. However, when compared to the replication method, the porosity created by direct foaming is generally less open resulting in lower permeability and higher strength.

1.3 Structure and properties of macroporous ceramics

1.3.1 The pore space and pore space accessibility

Macroporous ceramics with an open and interconnected pore space are established in a wide range of applications, such as diesel particulate filters, catalyst supports, and molten metal filters. Although the level of porosity and the pore size distribution are important characteristics of the porous structure, parameters such as the fraction of open porosity in conjunction with the degree of connectivity between the pores (cells) and the size of the pore openings (cell windows) have a strong effect on pore space accessibility. The fraction of open porosity describes the amount of the total porosity that is interconnected. The frequency of interconnections between pores, also described as the connectivity of the pore space, describes the number of neighbouring pores that are connected. The size of pore openings, also called cell windows or throats, often act as constrictions between connected pores to limit the flow of gas or fluid.

A high degree of connected porosity and a hierarchical pore size distribution is typically required for catalysis applications to achieve high permeability, accessibility to the active surface area and a low pressure drop. The pore size distribution, porosity and pore connectivity in porous ceramics can also be optimised for integration with living tissue in biomedical applications. In contrast, ceramic materials with a high porosity but low connectivity to minimise convective heat transport are suitable for thermal insulating panels for aerospace applications and kilns.
1.3.2 The solid material and mechanical properties

Macroporous ceramics are lightweight materials with high specific strength, compared to metal and polymer foams. The components of the solid material can be divided into struts, the walls separating the pore space, and vertices, where the struts join. The solid material is the load-bearing component whose shape, size and thickness influence the mechanical properties of the macroporous material. Typically the strength of macroporous ceramic materials increases with increasing density. The apparent density, $\rho/\rho_s$, where $\rho$ is the density of the porous material and $\rho_s$ is the density of the corresponding solid phase, is often used as an indicator of strength. For example, experimental results indicate that the Young modulus $E$ of a macroporous material relates to the apparent density:

$$\frac{E}{E_s} = C \left( \frac{\rho}{\rho_s} \right)^n,$$

(1.1 a)

where $E_s$ is the modulus of the solid material, $C$ a constant and $n$ an empirically determined exponent. This type of simplified estimation however fails to take into account the effect of micro-structural defects and the influence of the type of porosity (open or closed). In contrast, the models developed by Gibson and Ahsby for predicting the mechanical properties and behaviour of macroporous materials have proven more accurate. These models reduce the structural description of a porous material to consist of a lattice of solid struts surrounding a pore space, i.e a cell. The shape of the cells can be simplified to be e.g. cubically shaped, and the solid material can be described as a lattice, or a network of connected struts. The models describe the connectivity (topology) and shape of both the solid material and the pore space and manage to predict mechanical properties of macroporous materials.

1.4 Application of porous ceramic materials in carbon capture

Carbon capture and storage (CCS) has the potential to substantially reduce the combustion-related emission of CO$_2$ into the atmosphere. Previous work on CO$_2$-capture from flue gas has suggested that solid adsorbents could offer a more energy- and cost-efficient separation method in comparison to the commonly used amine-based liquids. Solid adsorbents commonly used for CO$_2$-adsorption are characterised by a high surface area and include e.g. activated carbon, silica gel, activated alumina, molecular sieves such as zeolites and mesoporous silica.
Swing adsorption processes use rapid changes in temperature or pressure, or both, to govern the separation and purification of gases from gas mixtures and typically employ packed beds made of an adsorbent material. However, the mass transfer properties and pressure drop across the adsorbent bed impart restrictions on the cycle time and hence the efficiency of the process. The adsorbents therefore need to be assembled into a structured material with a high adsorption capacity, good transport properties and necessary strength.

Recent work has suggested that hierarchically structured adsorbents have the potential to reduce the flow resistance of the permeating species and the pressure drop across the adsorbent material, which can shorten the cycle time thus allowing rapid swing adsorption processes. Tailoring the connectivity of micro/meso/macro-pores in a bulk structure has the potential to provide fast mass transport through macropores while maintaining a large surface area of the micro- and/or mesoporous constituents for improved performance.
2. Aims and objectives

This thesis demonstrates the synthesis and characterisation of macroporous alumina produced using a novel method with thermally expandable polymeric microspheres (EPS) to shape the macropores. The tailoring of macroporous ceramics poses the following questions: is the porous phase mainly open or closed; how does the porosity vary throughout the material; and, how well is the porous phase connected? Therefore, the first aim of this thesis was to establish suitable characterisation methods for the macroporous alumina materials. We focused our efforts on X-ray micro-computed tomography (µ-CT) and this study was presented in Paper I. Another aim was to explore more readily available alternative characterisation methods for macroporous ceramics. In Paper II we compared an evaluation of macroporous alumina using water-based porosimetry with evaluations by X-ray µ-CT analysis and mercury porosimetry.

A primary aim of this thesis was to establish a new and versatile manufacturing method for macroporous alumina based on the EPS as a templating material. To accomplish this, a powder vehicle system compatible with the spheres and their thermally induced expansion was formulated. We made use of the expansion of the EPS to shape the cast ceramics resulting in the processing method introduced in Paper III.

This thesis also aimed to control the connectivity of the pore space in the alumina materials and to characterise how permeability to fluid flow was affected. We therefore added a layer of alumina particles on the EPS and produced macroporous alumina materials with this modified templating material. A relationship was established between the sizes and characteristics of the connections between the pores and permeability to fluid flow. The resulting study is presented in Paper IV and includes 3D evaluation with X-ray µ-CT coupled to simulations of permeability to fluid flow.

A final aim was to apply the macroporous alumina materials as a support material for a microporous CO$_2$-adsorbent, zeolite 13X. The challenge was to establish a homogenous coating on the inner non-flat surface of the alumina substrate from a colloidal suspension of zeolite 13X and the binder (kaolin). This study was presented in Paper V. We also explored an alternative sacrificial templating route using carbon fibres and carbon spheres to produce hierarchically porous monoliths of zeolites presented in Paper VI.
3. Materials and methods

3.1 Materials and processing

The flow chart in Fig. 3.1 gives an overview of the processing steps for the preparation of the macroporous alumina materials presented in this thesis. We used thermally expandable polymeric spheres (EPS) as a templating agent to shape the pores in the macroporous alumina materials. The EPS are a commercial product (Expancel, Sweden) and consist of a co-polymer shell of acrylnitrile, methacrylate and acrylate and are filled with a blowing agent (isobutane). The EPS used for casting; 551DU40, 820DU40 and ON316WUX, have a mean particle size \( (D_{50}) \) of 10-16 \( \mu \)m (551DU40 and 820DU40) and 33 \( \mu \)m (ON316WUX), in the unexpanded state.

We coated some EPS of the type ON316WUX with a layer of alumina particles using a polyelectrolyte multilayer as a binder. We used the
following polyelectrolytes to achieve a stable particle coating: poly(ethylene imine) (ammonium salt, 99% purity, Mw = 10,000) abbreviated PEI; poly(acrylic acid) (sodium salt, 25 wt% in water, Mw = 50,000) abbreviated PAA; and poly(allylamine hydrochloride) (Mw = 60,000) abbreviated PAH. PAA and PAH were acquired from Polysciences Europe GmbH, Germany and PEI from Polysciences, Inc., U.S.A. The polyelectrolyte-coated EPS were coated with a layer of submicron sized alumina particles (AKP-30, Sumitomo Chemical Co., Ltd., Japan), and finished off with a last layer of PAA.

The macroporous alumina was shaped by gel-casting an alumina suspension containing a monomer and cross-linker together with the EPS. The EPS were either un-coated or coated with alumina particles. Upon heating, the polymeric spheres expanded and acted as a template for the pores. The monomer and cross-linker, which form a gel upon heating, preserved the porous structure created by the expanded spheres and the alumina particles. The organic materials were removed in air at 600 °C for a period of 3 hours prior to pre-sintering (1200 °C) or sintering (1500 °C) the macroporous alumina for 1 hour, respectively.

The suspension was based on the alumina powder AKP-30 (Sumitomo Chemical Co., Ltd., Japan) with an average particle size (D50) of 0.31 μm. The alumina powder was dispersed in the suspension with the polyelectrolyte Darvan 821A (Vanderbilt Company Inc., U.S.A.). We used methacrylic acid, abbreviated M-A, (Sigma-Aldrich Sweden AB, Sweden) and N,N’-methylenebisacrylamide, abbreviated MBAM, (Sigma-Aldrich Sweden AB, Sweden) as the monomer and cross-linker, respectively. The total amount of monomer and cross-linker with respect to water was 15 wt% and the weight ratio of M-A:MBAM was 6:1. Ammonium persulfate (APS) (Sigma-Aldrich Sweden AB, Sweden) was used as the initiator for the radical polymerisation of the monomer and cross-linker. The added APS corresponded to 4.75 wt% with respect to the total amount of monomer and cross-linker.

After the surface functionalisation with PEI, the macroporous alumina supports were coated with a microporous adsorbent by immersing the materials in a suspension of 20 wt% solids content of zeolite 13X (Luoyang Jianlong Chemical Industrial Co., LTD. Yanshi, Henan, China) and varying contents of kaolin (Sigma-Aldrich). A vacuum of 5 mbar was applied during the first 30 minutes to the macroporous alumina supports immersed in the colloidal suspension to impregnate the supports with the colloidal suspension. After drying, the coated supports were heat treated at a heating rate of 1 °C/minute up to 780 °C.

Hierarchically porous zeolite monoliths were produced from silicalite-1 (Süd-Chemie AG, Bruckmühl, Germany) and zeolite 13X powders with kaolin as a binder. Glassy spherical carbon (SPI-CHEM, West Chester PA, U.S.A.) and carbon fibres (SIGRI GmbH, Meitingen, Germany) were coated
with zeolite particles by a polyelectrolyte-assisted process using PEI and PAA and mixed with zeolite powders in suspension. The composite powder was dry pressed in a die of diameter 10 mm at an applied pressure of 10 MPa (Zwick GmbH Co & KG, Ulm, Germany) and heat treated at 550 °C to remove the carbon materials before consolidation at an elevated temperature.

3.2 Characterisation

3.2.1 Scanning electron microscopy
The scanning electron microscopy (SEM) was performed with a field emission gun scanning electron microscope (FEG-SEM) JSM-7000F (JEOL, Japan), with a JSM-820 (JEOL, Japan), or with a Zeiss UltraPlus FE-SEM.

3.2.2 Zeta potential
The zeta potential was measured with a Zetasizer Nano ZS instrument (Malvern Instruments Inc., London, UK). The standard deviation was calculated from the five zeta potential measurements and represented as error bars on each point.

3.2.3 Differential scanning calorimetry
The on-set temperature of the polymerisation was characterised by differential scanning calorimetry (DSC) (Perkin Elmer Pyris 1, Wellesley MA, U.S.A.) at a temperature increase rate of 5 °C/minute. The DSC measurements were performed on suspensions dispensed in stainless steel capsules (60 µL) sealed with an O-ring to suppress the evaporation of water during heating (LVC, Perkin Elmer). An empty capsule was used as a reference.

3.2.4 Thermo-gravimetry
Thermal gravimetric analysis was performed in technical air at a heating rate of 10 °C/minute (Perkin Elmer, Thermogravimetric Analyzer, TGA 7).

3.2.5 Thermo-mechanical analysis
Thermo-mechanical analysis (TMA) of the particle-coated and un-coated EPS was performed with a Mettler Toledo TMA/SDTA841e equipped with STARe software. The measurements were done in air at a heating rate of 20 °C/minute and with a net load of 0.06 N.
3.2.6 Evaluation of porosity and density
The porosity and density of the pre-sintered bodies were evaluated using water as immersion liquid. The macroporous ceramic body was dried to a constant weight at 120 °C and then cooled to room temperature in a desiccator. The dry porous body was weighed in air and then evacuated and infiltrated with distilled water which fills the open pores. The water-filled porous ceramic was weighed in air and the volume and open porosity of the porous body was calculated.

3.2.7 CO₂-adsorption
The CO₂-uptake measurements were performed on a Gemini 2375 (Micromeritics, U.S.A.) at 0 °C within a relative pressure region of 0.05-0.998 p/p₀ relative pressure. Prior to measurement, the as-received powder and thermally treated zeolite 13X-coated alumina supports were pre-treated under a flow of dry N₂ gas at a temperature of 350 °C for 8-10 hours.

3.2.8 Mercury porosimetry
The porosity and pore throat diameters of the porous alumina was evaluated by mercury intrusion porosimetry (Micromeritics AutoPore III 9410), assuming a surface tension (γ) and contact angle (θ) of mercury of 485 mN/m and 130°, respectively.

3.2.9 Water-based porosimetry
We evaluated the pore volume distribution of the macroporous alumina material with the water-based porosimetry (WBP) instrument TRI/Auto-porosimeter, version 2008-12 (TRI/Princeton, Princeton, U.S.A.) using water with 0.1% Triton X-100 as a liquid. Triton X-100, a non-ionic surfactant (γ = 30 mN/m), is a well-know wetting agent and we therefore assume full wetting of the liquid with the alumina surface (cos(θ) = 1). Fig. 3.2 shows a schematic view of the set-up for the water-based porosimetry. A contact between the macroporous alumina and an external liquid reservoir is established through a microporous membrane and a porous plate, situated inside the measuring chamber. Any uptake and release of liquid by the macroporous alumina from and to the liquid reservoir is detected by an analytical balance.

Prior to the WBP measurement the macroporous alumina material, cylindrically shaped with a diameter of 2 cm and height of 1 cm, was fully submerged in the working liquid and degassed in a desiccator to assure complete impregnation of the alumina material with liquid. The liquid-filled macroporous alumina was thereafter placed in the WBP chamber and the
pressure (P1) was increased. Increasing the pressure inside the chamber causes a pressure difference between the liquid inside the chamber and the liquid reservoir, which is at an ambient pressure (P2). Applying a pressure at the air-water interface will force the water to drain when the capillary pressure of a narrow passage is exceeded. The narrowest passages along a channel of connected pores will limit the release of water and define the apparent throat radius. The uptake of water, on the other hand, is limited by the widest passages along a channel of connected pores and thus defines the apparent pore radius.

![Diagram of the set-up of the water-based porosimetry instrument](image)

**Fig. 3.2.** Sketch of the set-up of the water-based porosimetry instrument.

### 3.2.10 X-ray micro-computed tomography

The X-ray micro-computed tomography (µ-CT) instrument operates with a cone beam geometry and was developed and built at the Australian National University. Cylinders with a diameter of 5 mm were extracted from the middle of macroporous alumina blocks and imaged with the X-ray source operating at 80 kV and with a beam current of 100 µA. For the 2048³ voxel tomograms, a set of 2880 two-dimensional (2D) radiograph projections were acquired at different rotation angles covering the complete 360°. A 1 mm thick dense aluminium filter was placed in front of the alumina cylinder to reduce the problem of beam hardening of the polychromatic beam, which may lead to artefacts in the radiographs. The resulting voxel dimension was 3 µm.

The 2D radiographs were first pre-processed to minimise artefacts and then reconstructed with a Feldkamp algorithm to generate a tomogram consisting of voxels.

### 3.2.11 Simulation of permeability

The permeability was calculated on the segmented 3D data by using a lattice-Boltzmann (LB) method. The LB approach is a mesoscopic
numerical method used in computational fluid dynamics, where the macroscopic dynamics of the solution of a discretised Boltzmann equation match the Navier-Stokes equation. For computational reasons, the simulations were conducted on independent sub-domains from each macroporous alumina data-set with sizes between $724^3$ and $1440^3 \mu m^3$. The sub-volumes have dimensions six times larger than the mean pore size, which has been shown to be sufficient for accurate estimations of the permeability.$^{70,71}$ The permeability of each sub-volume was calculated by applying a small pressure gradient to the liquid in one direction.$^{72}$

For computational simplicity, the outer boundaries of the sub-volume parallel to the applied pressure were modelled according to the mirror-image boundary condition, and the outer boundaries perpendicular to the applied pressure were saturated by a thin layer of liquid. In the direction of flow, the liquid medium was made quasi-periodic; any liquid exiting the porous body re-entered at the opposite face.$^{70}$ We also assume the no-slip boundary condition at the solid-fluid interfaces.$^{69}$
4. Results and discussion

4.1 Three-dimensional visualisation and mapping of the macroporous space

4.1.1 Introduction

The structure of macroporous ceramics is traditionally characterised by two-dimensional (2D) imaging techniques and intrusion methods, such as mercury porosimetry. The imaging techniques include light microscopy and electron microscopy combined with image analysis or image reconstruction procedures.\textsuperscript{73,74} Although these methods provide high resolution information on the local (surface) structure, arbitrary planar intersections of a pore space mostly fail to provide accurate information on the spatial morphology. Since 2D images do not capture spatial variations (e.g. pore size distribution, gradients, etc) and spatial orientations (e.g. pore shape), the ability to extract statistically significant three-dimensional (3D) information about the bulk material is therefore limited.\textsuperscript{73} 3D data can be extracted by serial sectioning followed by volumetric reconstruction, e.g. by combining focussed ion beam (FIB) with scanning electron microscopy (SEM).\textsuperscript{75} However, the manipulation of the material is destructive and only small volumes can be analysed.

Confocal laser scanning microscopy (CLSM), a non-destructive imaging technique, can in principle obtain and reconstruct 3D information, providing that the material is sufficiently transparent.\textsuperscript{74} Even though the refractive index of most ceramic materials is too high for CLSM, it has been demonstrated that immersing fluids with similar dielectric properties as the solid can reduce scattering sufficiently to allow 3D information to be retrieved.\textsuperscript{76,77} 3D information is particularly important for characterising the connectivity, transport and accessibility properties of porous solids, such as human bone. X-ray micro-computed tomography (µ-CT) and magnetic resonance imaging (MRI) are non-destructive techniques which allow structural characterisation of heterogeneous materials. X-ray µ-CT provides good spatial resolution whereas MRI is suitable for materials with a high level of water content; MRI therefore gives a good contrast resolution for soft tissues of the body.\textsuperscript{78,79}
The aim of this chapter was to compare qualitative and quantitative aspects of the porous structure retrieved with different techniques: X-ray \( \mu \)-CT, scanning electron microscopy images and two intrusion methods (mercury porosimetry and water-based porosimetry (WBP)).

4.1.2 Three-dimensional characterisation of macroporous materials with X-ray micro-computed tomography

X-ray \( \mu \)-CT provides 3D information about heterogeneous materials and it has progressed from being a qualitative imaging technique used in medical science\(^74\) to become a sophisticated structural analysis method in materials science.\(^{80-83}\) The use of X-ray \( \mu \)-CT is especially appropriate for the characterisation of porous materials, due to the distinct difference in the attenuation coefficient between the solid and gaseous (void) phases. A wide range of porous materials and cellular structures have been characterised with X-ray \( \mu \)-CT: ceramics, concrete, metals, and various organic materials such as polymers, food stuff and materials for tissue engineering.\(^{84-88}\)

A wide range of inherent 3D structural parameters of a macroporous material can be analysed and quantitatively evaluated from X-ray \( \mu \)-CT data, such as volume fraction of the solid and pore phases, pore and throat size distributions, wall thickness and the interconnectivity of the respective phases.\(^{81,84,89}\) Studies have shown that quantified structural parameters derived from X-ray \( \mu \)-CT data are in good agreement with other techniques, if the resolved length scale is smaller or equal to the important structural features of the material.\(^{84,85,89}\)

Characterisation with X-ray \( \mu \)-CT also offers a unique possibility to relate the material structure to processing conditions, e.g. in foams of various compositions,\(^{41,82,86,90}\) and to follow structural changes during mechanical testing and heat treatments.\(^{80,83,91}\) Macroscopic bulk properties, such as permeability, mechanical properties and conductivity, can be numerically simulated on the 3D data provided by X-ray \( \mu \)-CT.\(^{71,72,84}\) Previous work has shown that the simulated results for different classes of porous materials are in good agreement with experimental results.\(^{70,71}\) Numerical simulations of fluid flow in a porous structure provide information on e.g. flow paths and interactions between multi-phase fluids;\(^{41,69,70,72}\) properties that are difficult to measure experimentally. Simulations of fluid flow on X-ray \( \mu \)-CT data of porous rocks in combination with NMR analysis can also improve the characterisation and simulation of two-phase flow.\(^{92}\)

4.1.3 Acquiring images with X-ray micro-computed tomography

In X-ray transmission tomography, an object is scanned with X-rays at multiple rotational increments and a detector measures the decrease in X-ray
intensity at each projection. The attenuation of X-rays travelling through an object is described by Beer-Lambert’s law, and in the case of multiple materials the final X-ray intensity $I$ adds up to:

$$I = I_0 \exp \left[ \sum_i (-\mu_i x_i) \right],$$  

(4.1 a)

where $I_0$ is the initial X-ray intensity, and each increment $i$ reflects a single material with the attenuation coefficient $\mu_i$ with linear extent $x_i$. At each incremental step a 2D image, a radiograph, is recorded of the transmitted and attenuated X-ray intensity. The radiograph is later used to create a map of the 3D density function of the object. The attenuated intensity is strongly dependent upon the X-ray energy. For a monochromatic X-ray source (a synchrotron) this equation can be solved directly, but for a polychromatic X-ray source (lab-based CT) the complete solution requires solving the equation over the range of the X-ray energy spectrum utilised.

A polychromatic beam may lead to beam-hardening artefacts, i.e. changes in image grey levels caused by differential attenuation (preferential attenuation of low energy X-rays) of photons within the investigated material. As a result of a polychromatic beam the mean energy of X-rays will gradually increase along the path through a material, and the measured values of the attenuation coefficient $\mu$ will be lower at the centre of a material. These artefacts can be reduced by pre-filtering the X-ray beam, typically with a filter of the same composition as the major composition material of the object.

$^{67,93}$

The spatial resolution of the final 3D X-ray $\mu$-CT data is mainly determined by the focal spot size, the size and number of the detector elements, and the distances between the source and object; and object and detector. A decreased focal spot size comes at a cost of reduced X-ray intensity, which affects the signal-to-noise ratio and thus image clarity. Commonly the source-to-detector distance is fixed and the maximum in-plane resolution is achieved by minimizing the source-to-object distance. The accuracy of the mechanical stage settings must exceed that of the expected resolution, and therefore piezoelectric controlled stages are often used. The choice of photon energy is also important as low energy photons deliver high contrast images but with higher relative noise due to increased scattering.

There are three main types of beam configurations for the instrumental set-up for X-ray tomography, shown in Fig. 4.1: planar fan beam, cone beam and parallel beam configuration. In planar fan beam (Fig. 4.1(a)) the X-rays are collimated to reduce the scatter of the X-ray beam and its negative effects, but data can therefore only be acquired for single slices. In the cone-beam configuration (Fig. 4.1(b)) a planar detector acquires data for an entire
object during each scan in rotational increments. This corresponds to several hundreds or thousands of images acquired. Cone-beam acquisition has some problems with blurring and distortion, and is also more subject to artefacts stemming from scattering if high-energy X-rays are utilised. A low photon flux source, such as a lab-based X-ray source, demands long exposure times and requires a detector which delivers a very low level of noise. The signal to noise ratio can be reduced by increasing the acquisition time at each incremental position. Helical cone beam tomography is a variant of the cone-beam data acquisition in which the data are acquired as either the X-ray source or the scanned object travels in a spiral trajectory along the vertical axis. Helical cone beam tomography allows scanning larger volumes, but requires quite different and more complex reconstruction algorithms.

A parallel beam (Fig. 4.1(c)) can only be achieved at a synchrotron source beam line. The X-ray intensity (flux of photons) of a synchrotron source is very high and this allows quick data acquisition with no or little distortion, a low signal to noise ratio and high spatial resolution. The monochromatic beam achieved at a synchrotron also enables quantitative measurements of the absorption coefficient $\mu$ and thus quantification of material densities. No magnification can be achieved with this set-up and the spatial resolution thus mainly depends on the resolution (effective pixel size) of the detector. The object to be imaged is limited in size, depending on the beam line configuration and the X-rays are generally of low energy (<35 keV), which may exclude imaging of materials with a high atomic number (Z).

After image acquisition with transmission X-ray tomography the 2D radiographs need to be reconstructed into a digital 3D image (tomogram) of the scanned material. The intensity data are first pre-processed to compensate for a polychromatic beam and to detect and correct errors, such as variations of the X-ray flux and mis-alignment of the scanned material. With a back-projection formula the data acquired at each incremental step are back-projected across a volumetric grid of voxels, along the same angle as it was acquired, and successively superimposed with all back-projections. A simple back-projection results in radial blurring, compared to the correct image, but this can be reduced by applying a convolution filter to each image before back-projection. The Feldkamp algorithm is a convolution-
backprojection formula developed for the direct reconstruction of 2D projections from fan-beam transmission X-ray tomography data, later generalised to cone-beam data. This algorithm can be combined with the Fourier Slice Theorem to significantly reduce the computational cost of the reconstruction. The Fourier Slice Theorem is a next-generation reconstruction method in which Fourier transforms are used to perform the convolution in filtered back-projection.

4.1.4 Image analysis and pore space identification of reconstructed X-ray tomogram data

The analysis of grey-scale X-ray µ-CT tomograms of porous and composite materials is a challenge since features at or below the instrument resolution will blur sharp edges at phase boundaries. Therefore the tomogram data, which are presented in grey levels corresponding to the X-ray attenuation, is treated with image enhancing filters to reduce noise and blur. We used two different filters in sequence: a denoising anisotropic diffusion filter and an edge sharpening “unsharp mask” filter.

![Fig. 4.2. X-ray micro-computed tomography intensity histogram, and grey-scale and binarised two-dimensional representations.](image)

In (a) the intensity histogram of the entire tomogram shows a significant difference in X-ray attenuation between the two phases: pore (left peak) and solid (right peak). The cut-off values for the segmentation seeding regions of the two phases are indicated by the dotted lines. (b) shows the reconstructed grey-scale tomogram slice and (c) shows the binarised result after segmentation where white represents the solid ($\text{Al}_2\text{O}_3$) and black the porous phase.

It should be noted that before the 3D-imaging of the macroporous alumina all organic additives were removed and the materials were pre-sintered. Hence, the ceramic materials only contain two phases: alumina and air. The voxel intensity histogram in Fig. 4.2(a) shows that it is possible to identify two distinctive peaks that represent the two phases. For further analysis, the voxelated data need to be categorised as either solid or void; this process is called segmentation. In this work the segmentation was performed with a method known as ‘converging active contours’, which is a combination of a
watershed transform and the active contour method. This approach is based on user-defined “seeding regions” for each phase. Two cut-off values close to the intensity peaks were selected; everything below the lower limit is designated as pore and everything above the upper limit is designated as solid (Fig. 4.2(a)). The intensity values between these cut-off boundaries were assigned to each binary phase by the converging active contour method. Figs. 4.2(b) and 4.2(c) show a comparison of a grey-scale tomogram slice with the binarised result after segmentation.

We used scanning electron microscopy (SEM) to qualitatively evaluate the limits of the X-ray µ-CT method. This verified our ability to accurately capture the morphological features of the porous materials. The dimensions of a voxel in the X-ray µ-CT images was 3 µm, which is thus the size of the smallest pore or feature visible in these images. Fig. 4.3 shows a comparison of an SEM image with 2D slices from different stages in the treatment of the X-ray µ-CT data. The data were selected from the same position in a macroporous alumina material with an average porosity of 51%. An algorithm aligned the SEM image to identify the corresponding 2D slice in the 3D data-sets of the grey-scale tomogram and segmented data. We found that the shape of the pores was very well reproduced in the segmented X-ray µ-CT image, whereas the fine features of e.g. some pore walls could not be captured in detail.

Fig. 4.3. Comparison between a scanning electron microscopy (SEM) image and two-dimensional X-ray micro-computed tomography (µ-CT) representations of a macroporous alumina with an average porosity of 51%. (a) shows the SEM image, which can be compared with the corresponding X-ray µ-CT data at different stages of the analysis: (b) the grey-scale tomogram, (c) the binarised data after segmentation and (d) after identification and labelling of the individual pores.

The next step in the 3D analysis is to identify the pores and the pore throats in the segmented data. This is necessary before a quantitative analysis of the
characteristics of the pore network in the alumina material can be performed. The identification was based on an Euclidean distance map, which associates to each pore voxel the nearest distance to a solid phase voxel.\textsuperscript{96} A watershed transform, applied to this distance map, partitioned the pore space into pore bodies by expanding from a seed voxel situated at each pore centre and thus identifying each individual pore space.\textsuperscript{96,97} A pore merging algorithm is applied to the partitioned pore space to reduce any over-partitioning. As the watershed algorithm considers the 3D structural information of a pore space, it can divide a large porous region into several distinct pores. Fig. 4.3(d) shows a 2D slice of the pore structure in which the pores are identified and individually coloured.

4.1.5 Pore network identification and three-dimensional visualisation

Once the data have been processed and distinct pores have been identified and labelled, a network model can be created. A network model allows the 3D connectivity and pore/throat characteristics of the material to be defined. The pore throats, which are the open connections between the pores, are identified as the narrowest constriction between two connecting neighbouring pores.\textsuperscript{96,98,99} Thereafter, a pore network is generated using a refined medial axis transform.\textsuperscript{96,100,101}

Two different methods to visualise the 3D data-sets are illustrated in Fig. 4.4. Figs. 4.4(a) and 4.4(c) show segmented volume visualisations of two different macroporous alumina materials; the schematic stick-and-ball illustrations in Figs. 4.4(b) and (d) are the respective representations of the connected pore network. In this schematic illustration, pores are shown as spheres while throats are represented by cylinders. The centre of the sphere corresponds to the centre of geometry of the pore, while the diameter is proportional to the diameter of the largest sphere that can be inscribed within the pore.\textsuperscript{81,101} The diameter of the cylinders correspond to the diameter of the throats. The number of cylinders connected to each sphere also illustrates the number of connected pore neighbours. The network models are visualised using Drishti, a volume visualisation program developed at the Australian National University.\textsuperscript{98,102} Note that the geometric representations in Figs. 4.4(b) and 4.4(d) only are schematic illustrations of the network topology; the throats are pictured as straight cylinders, even if that is not the case in reality.
Fig. 4.4. Three-dimensional representations of macroporous alumina materials with an average porosity of 76% (a, b) and 51% (c, d). In (a) and (c) the representations are based on segmented data. The surface of the pores is highlighted with a yellow colour, whereas the solid phase in orange is slightly transparent to increase visibility. In (b) and (d) three-dimensional network model images show how the pores, here pictured as spheres, are connected by throats, represented by cylinders. Only spheres with centres inside the cube are shown. All the data-sets are 1160x1160x580 µm\(^3\) in size.

4.1.6 Visualising the variation of porosity

The spatial variation of porosity is shown in Fig. 4.5 for four macroporous alumina (MA) materials templated with expandable polymeric microspheres (EPS) with different average porosities. Fig. 4.5 shows how the porosity varies in the z-direction, which corresponds to the direction perpendicular to the bottom of the mould used for casting the alumina materials. We find that the spatial variation of the porosity is significantly smaller for the highest...
porosity (76%) macroporous alumina (MA) materials templated with EPS (MA-EPS-76), compared to the lower porosity (46%, 51% and 57%) macroporous alumina materials templated with EPS (MA-EPS-46, MA-EPS-51, and MA-EPS-57).

The 2D slices in Fig. 4.5 show that the regions with maximum porosity in the low-porosity materials (MA-EPS-46 and MA-EPS-51) contain much larger pores and a more inhomogeneous distribution of the solid phase and the pores, compared to the high-porosity material (MA-EPS-76). We speculate that the expandable spheres are able to expand more when a relatively low amount is added compared to high additions when crowding restricts the expansion.

Fig. 4.5. Spatial porosity fluctuation in the z-direction of macroporous alumina materials with an average porosity of 76%, 57%, 51% and 46%, respectively. (The suffix in the material label refers to the average porosity of the material.) The profile of the pore phase fraction in the segmented 3D data are plotted as a function of height, and is matched with 2D images, on the right hand side, that display slices with maximum and minimum porosities for each material. In the 2D images white represents the solid phase and black represents the porous phase (void).

4.1.7 Comparing X-ray micro-computed tomography with porosimetry methods

We have used two other methods, mercury porosimetry and water-based porosimetry (WBP), to determine the porosity, pore size distribution and throat size distribution. The data obtained with these methods were compared with information on the total porosity and the open (connected) porosity from the segmented X-ray µ-CT data-sets. Fig. 4.6 shows that the porosity determined with mercury porosimetry from pores equal to and larger than the voxel resolution (3 µm) correlates very well with the open
porosity determined from X-ray µ-CT. The correlation between the X-ray µ-CT and mercury porosimetry data holds over a porosity range between 40% and 80%, in which the open porosity is found to depend linearly on the amount of expandable spheres added to the gel-casting suspension.

Fig. 4.6. Comparison of the open porosity from the X-ray micro-computed tomography (µ-CT) with the porosity from pores of diameter \(\geq 3\) µm from the mercury (Hg) porosimetry. The porosity is plotted as a function of varying amounts of added expandable microspheres on a dry weight basis (DWB).

Mercury, a non-wetting liquid \((\cos(\theta)<1)\), is used for porosimetry by forcing this liquid into a porous material. The smallest constrictions between the pores, the throats, present the highest capillary pressure and thus restrict the entry of mercury into the network of pores. Mercury porosimetry therefore probes the throat size distribution in intrusion mode.

Water is a wetting liquid \((\cos(\theta)\geq 1)\) and spontaneously fills the voids of a network of pores. Applying a pressure at the air-water interface will force the water to drain from a macroporous body when the capillary pressure of a constriction in its pore space is exceeded. The narrowest passages along a channel of connected pores will limit the release of water and define the apparent throat radius. The uptake of water, on the other hand, is limited by the widest passages along a channel of connected pores and thus defines the apparent pore radius.

The throat size distribution of the macroporous alumina was evaluated in extrusion mode on the pre-filled macroporous alumina using WBP (Fig. 4.7(a)). This size distribution reflects the throats which resist drainage of liquid. In comparison, the throat size distribution calculated from the X-ray µ-CT data (Fig. 4.7(a)) represents all constrictions in the macroporous alumina. The apparent ‘noise’ in this size distribution is simply an artefact of a higher sampling rate.

The pore size distribution of the macroporous alumina was evaluated in intrusion mode using WBP. It overlaps well with the pore size distribution
from the X-ray µ-CT data for pore diameters between 65 and 180 µm (Fig. 4.7(b)). The WBP indicated a presence of pores with sizes up to 1200 µm, contrary to the pore size distribution from the X-ray µ-CT data which indicated that the diameter of the major parts of pores in the macroporous alumina was limited to below 400 µm. In WBP these wide passages act as restricting passages in a channel of connected pores and as these passages fill the connected pores will also fill. Therefore the volume of the largest pores is overestimated in the WBP pore size distribution.

Fig. 4.7. In (a) the throat size distribution, and in (b) the pore size distribution in the macroporous alumina, evaluated by water-based porosimetry and X-ray micro-computed tomography (µ-CT).

4.2 Thermally expandable polymeric microspheres: A novel templating material for macroporous alumina

4.2.1 Introduction

Many processing methods have been developed to create macroporous ceramics, each with its limitations with respect to the characteristics of the porous structure, such as the level of porosity, the type of porosity (open or closed) and the pore size distribution.\textsuperscript{12} The aim of the work presented in this chapter was to explore the potential of a novel sacrificial templating route that utilised the combination of gel-casting with thermally expandable polymeric microspheres. The temperature range for the gel-casting process had to be tuned to allow the gas-filled polymer spheres to expand prior to the setting of the powder body. We studied how the porosity and the pore size distribution in the final material could be tailored by controlling the amount and size of the expandable microspheres. It was also demonstrated how the temperature induced expansion of the microspheres was used to directly cast macroporous bodies of a near-net complex shape with detailed surface patterns.
4.2.2 Gel-casting

Gel-casting is a near-net shape technique for ceramic\textsuperscript{103-106} or metal\textsuperscript{107} materials. It was originally developed to create dense ceramics as an attractive alternative to wax-based injection moulding.\textsuperscript{34,104} The process is based on the casting of an aqueous slurry with ceramic powder and water-soluble organic monomers. After casting the polymerisation of the monomer system, commonly a monomer and a cross-linker, is initiated by e.g. heating or a change in pH.\textsuperscript{108} The monomer and cross-linker form a polymer network – a gel – throughout the cast ceramic body, and the result is a homogenous green body of high strength.\textsuperscript{109} After drying the cast ceramic body is heated to burn off the organic components and then sintered.

The gel-casting slurry is a vehicle for the ceramic powder and facilitates homogenous mixing and enables casting of the components. A low viscosity slurry is beneficial for both mixing and casting in slurry processing and needs to be combined with high solids loading to reduce shrinking and the risk of crack formation during drying.\textsuperscript{110,111} Originally, the gel-casting process was based on water-soluble monomers and cross-linkers such as the monofunctional acrylamide and difunctional methylenebis-acrylamide.\textsuperscript{104} The gel-casting process was not a success in industry at first since the acrylamide monomers are neurotoxic. Since then casting-processes for ceramics have been developed with less toxic\textsuperscript{112,113} and more environmentally friendly binders like albumine\textsuperscript{114} and agarose.\textsuperscript{115}

Gel-casting is similar to slip-casting and injection moulding but holds several advantages. It is an aqueous process with very low amounts of organics; typically 4 wt% in a dry body\textsuperscript{104} compared with up to 30 wt% binder in injection moulding.\textsuperscript{116} It should be noted that the strength is still high enough to allow green machining, even though the binder content is low in comparison.\textsuperscript{107} The low binder content makes the debinding step less critical and reduces the risk for inducing cracks.\textsuperscript{117} Gel-casting can be used for prototypes and small series as well as for automated production. Different mould materials ranging from metals, glass, wax and plastics\textsuperscript{117} can be used and complex shapes\textsuperscript{105,117-119} can be cast to achieve near-net shape.

4.2.3 Gel-casting with thermally expandable spheres

In this work we have used thermally expandable polymeric microspheres (EPS) as a sacrificial template together with a gel-casting suspension for direct casting of macroporous ceramic bodies. The commercially available microspheres have already found industrial use in polymer-based applications such as acoustic insulation and to reduce the weight in vehicles.\textsuperscript{120} The expansion of the polymeric microspheres has also been used to control the flow in microfluidic systems.\textsuperscript{121} The EPS consist of a polymer shell which softens with increasing temperature as the glass transition temperature
of the thermoplastic copolymer is reached. Parallel to this process, the liquid hydrocarbon encapsulated inside the gas tight shell will expand and thus increase the internal pressure of the microspheres. These two coupled processes, the softening of the polymer shell and the increase of the internal pressure induce a dramatic volume expansion of more than 40 times when the temperature becomes sufficiently high.

According to the thermal mechanical analysis (TMA) performed in air by the supplier, the three different expandable microspheres used in this work are expected to start to expand at 76-81 °C (820DU40), 88 °C (ON316WUX) and 95-100 °C (551DU40) respectively. The difference in the expansion temperature is related to variations in the co-polymer composition and the corresponding glass transition temperature of the thermoplastic shell. It should be noted that the expansion temperature is related to the heating rate and that the TMA data were obtained at a relatively high heating rate of 20 °C/minute. We have found that the microspheres expand also at temperatures slightly below the specified on-set temperature at a heating rate of 5 °C/minute and that the chosen process temperature of 80 °C is sufficient to expand the microspheres in suspension if the temperature is held at least 25 minutes.

Catalysts are often added to gel-casting systems to reduce the on-set temperature of polymerisation of the monomer and cross-linker. The catalyst TEMED (\(N,N,N,N'\)-tetramethylethylenediamine) is commonly added when the gel-casting process is based on the monomer cross-linker system M-A:MBAM.\(^{122}\) This is the system we have consistently used for casting with the EPS. We have chosen not to add any catalyst, which increased the polymerisation temperature of the gel-casting suspension, and to adjust the amount of initiator to tune the on-set temperature of the gel-casting suspension. Fig. 4.8 shows that by optimizing the amount of initiator (APS) it is possible to achieve an on-set of the gel-casting/polymerisation reaction close to 80 °C (at a heating rate of 5 °C/min). Polymerisation is an exothermic reaction and its on-set temperature is defined as the intersection of the baseline with the extrapolated linear section of the ascending peak slope.

It is essential that the setting and consolidation of the concentrated ceramic powder suspension does not occur prior to the maximum expansion of the microspheres to avoid the build-up of internal stresses that can lead to cracking and warping. A low process temperature of 80 °C was chosen to be able to control the microsphere expansion and minimise problems related to water evaporation.
Fig. 4.8. Differential scanning calorimetry (DSC) measurement (heating rate 5 °C/min) of the alumina gel-casting suspension. The graph displays the heat flow (mW) as a function of temperature (°C), where a positive signal is equivalent to an exothermic reaction. The striped area indicates the temperature range for the on-set of microsphere expansion.

One of the advantages of using expandable microspheres as a sacrificial template material is that the total amount of organic material is relatively low, even at final porosities of 80% or above. The thermo-gravimetric data in Fig. 4.9 show that the total weight loss is relatively small and remains below 5 wt% even when a large amount of expandable microspheres is added to reach a final porosity of 72.5%. In fact, it is the polymerised monomers and cross-linker that constitute the major source of the organic additives in the cast bodies, amounting to about 4 wt% with respect to the alumina. It is sufficient to add less than 1-2 wt% of EPS to achieve a material with a final porosity of above 80%.

Fig. 4.9. Thermo-gravimetric (TG) analysis (heating rate 10 °C/min) in dry air of alumina green bodies at various final porosities: 62.7% and 72.5%, respectively.
4.2.4 Effect of the amount and size of the expandable microspheres on the porosity and pore size

Fig. 4.10 shows typical fracture surfaces of alumina bodies with porosities ranging from 71% to 86%. The expandable microsphere 820DU40 was used to produce the porous material in Fig. 4.10(a) while ON316WUX was used to produce the materials with a highly interconnected porous phase in Figs. 4.10(b), 4.10(c) and 4.10(d). It is clear that the internal pressure in the expanding microspheres is sufficient to result in unconstrained expansion that yields spherical pores after template removal. The pores are homogenously distributed and the struts (pore walls) are dense.

![Fig. 4.10. Scanning electron microscopy images of fracture surfaces of porous alumina bodies where microspheres of different sizes were used to create macroporous bodies of similar porosity: (a) 83.7% and (b) 82.4%. In (a) the mean microsphere size in the unexpanded state is 10-16 µm and in (b) the mean microsphere size in the unexpanded state is 33 µm. Representative images are shown of (c) a cell window with a thin wall of single alumina grains, and (d) of dense pore walls separating three pores.](image)

The pore walls are generally thin in these highly porous alumina bodies; see e.g. Fig. 4.10(d). Comparison of Fig. 4.10(a) and (b) suggests that the use of a smaller microsphere results in smaller pores and that the associated pore walls are thinner compared to the materials with larger pores. Indeed, simple geometric considerations suggest that the (average) wall thickness should be inversely related to the pore size at equal porosities. When the amount of microspheres becomes sufficiently high, it is observed that a significant fraction of the pores are connected; hence the porosity becomes more and more open as the total porosity increases. As the microspheres are squeezed together the alumina grains are forced aside and eventually leave a hole, see e.g. Fig. 4.10(c). The contact area between two microspheres that are forced
together will be circular or oval, which explains the shape of the cell windows.

Fig. 4.10 also illustrates that the pore size distribution can be controlled by using expandable microspheres of different sizes. The pores originating from the expandable sphere ON316WUX with an initial diameter ($D_{50}$) of 33 µm (before expansion), shown in Fig. 4.10(b), are significantly larger than the pores obtained with the expandable sphere 820DU40 with an initial diameter of 10-16 µm (Fig. 4.10(a)).

Fig. 4.11 shows that it is possible to tune the porosity and relative density by simply controlling the added amount of the EPS to the alumina suspension; the porosity clearly scales with the amount of added microspheres (ON316WUX). We find that the results from mercury porosimetry show slightly lower porosities compared to the water immersion measurements. This is not surprising considering that water will wet the alumina and thus enter smaller pores than mercury. The closed porosity derived from water immersion measurements is below 2.5%.

![Graph showing porosity and relative density](image)

**Fig. 4.11.** Open porosity and relative density in pre-sintered porous alumina evaluated by water immersion and mercury porosimetry as a function of amount of added expandable microspheres in wt% dry weight basis (dwb). The inset shows Equation (4.2 b) fit to the data points corresponding to water porosimetry, plotted with the same axes.

Fig. 4.11 shows that the open porosity increases with the amount of added EPS following a non-linear relationship. The pore volume generated by the microspheres in the pre-sintered alumina can be expressed as the quotient of the amount of added microspheres in wt% ($x$) and the density of the expanded microspheres ($y$) in g/cm$^3$, assuming a density of 4.0 g/cm$^3$ for alumina. The total porosity ($P$) has two contributions: the porosity generated by the microspheres ($x/y$), and the porosity originating from the inter-particle voids in the pre-sintered alumina ($P_0$). This can be expressed as:
\[ P = \frac{x + P_0 \cdot 25}{y + \frac{P_0 \cdot 25}{1 - P_0}}, \quad (4.2 \text{ a}) \]

which by rearrangement yields:

\[ P = P_0 - \frac{(P_0 - 1)^2 x}{(P_0 - 1)x - 25y} \quad (4.2 \text{ b}) \]

The inset in Fig. 4.11 shows the porosity (%) evaluated with water immersion as a function of added microsphere content (wt%), plotted together with Eq. 4.2 b. We find that the increase in porosity as evaluated by water immersion follows the prediction of increase in porosity from Equation (4.2 b) well. Equation (4.2 b) yields a porosity of pre-sintered alumina (without any addition of expandable microspheres) of 27% and a microsphere density after expansion (y) of 0.01 g/cm³.

4.2.5 Zero external pressure injection moulding: utilizing the internal volume expansion for direct casting of complex shaped macroporous bodies

The volume expansion of the microspheres provides a possibility to use this novel casting technique to produce near-net shaped macroporous bodies. The process proceeds in a manner very similar to baking; the microsphere expansion induces a volume expansion where the suspension eventually fills the mould and the parallel gelation of the monomer and cross-linker consolidates the expanded suspension. Hence, it is possible to partially fill a mould with the suspension that contains the unexpanded microspheres, close the mould and then heat it to induce the microspheres to expand and thus force the suspension to fill the mould. The suspension then sets when the monomers and cross-linkers polymerise. Fig. 4.12 illustrates different types of macroporous alumina bodies that can be cast by this novel near-net shape casting technique. The excellent replication of the surface features suggests that the internal pressure that the microsphere expansion induces is sufficient for the suspension to completely fill the mould prior to setting. By inspecting the global pore distribution of the cast bodies we observed that the largest macropores were concentrated to the upper, dome-shaped part of the cast cylinders.
Fig. 4.12(d) is an attempt to schematically describe how the suspension fills a cylindrical mould as the microspheres expand. The suspension increases in height much like a baking cake generating a dome-shaped top. We have utilised this effect to create a porous monolith with a hierarchical porosity (Fig. 4.12(b)). A cylinder containing several cylindrical rods aligned with the axis of the cylinder was filled to one fifth volume with the pore-forming suspension. Heating the suspension induced a volume expansion around the cylindrical rods. Burning out the organic templating material yielded a material with porosity at three different length scales; the cylindrical channels were the largest pores, the intermediate porosity stemmed from the sacrificial EPS and there were also macropores with a much smaller pore size distribution that originated from the interstices between the pre-sintered alumina grains.

Fig. 4.12. Macroporous bodies of both cylindrical and complex shape that have been produced using the gas-filled microspheres as an expandable pore former in the gel-casting suspension. (a) demonstrates that the surface patterns of an acrylonitrile butadiene styrene (ABS) mould (contact lens container) has been reproduced with great detail. (b) shows that a pattern of elongated channels are integrated into the macroporous, gel-cast material. (c) shows a cylindrical body that has been cast in a high-density polyethylene mould with the surface details well reproduced. (d) shows how the level of a suspension that contains a significant amount of expandable microspheres varies with time; prior to heating (0 min); when the suspension first reaches 80 °C (25 min) and when expansion is complete (45 min).

4.3 Permeability of macroporous ceramics

4.3.1 Introduction

Controlling the transport properties of macroporous ceramics is essential for many applications, ranging from filtration, catalyst supports and to biomedical implants, and each application has specific requirements for the macroporous material with respect to its porous structure and the required permeability. However, there are few processing methods for macroporous ceramics as well as few characterisation methods which allow versatile tailoring and analysis of the porous structure and the resulting permeability.
The aim of the work presented in this chapter was to develop a new route for regulating the permeability to fluid flow in the macroporous alumina materials. We simulated the permeability to fluid flow on three-dimensional (3D) data-sets retrieved with X-ray µ-CT and compared these results to predictions based on the Katz-Thompson model.\textsuperscript{124}

### 4.3.2 Permeability of a macroporous material

Permeability describes the transport of a fluid or gas through a porous material. The permeability is influenced by structural features of the porous structure e.g. the level of porosity, the type of porosity (open or closed) and the pore size distribution. Other parameters such as the tortuosity, the degree of connectivity between the pores, and the size of the constrictions between these connected pores (throats) also have a strong effect on the pore phase accessibility and permeability to gas or fluid flow.\textsuperscript{10,22,23,41,43} These parameters are not easily quantified with established methods like mercury porosimetry and scanning electron microscopy. 3D information from X-ray µ-CT, however, can be used to determine the above mentioned structural parameters and to simulate the permeability.\textsuperscript{125-128}

The permeability to fluid flow through a porous material is commonly described using either of the two main equations: Darcy’s law (Eq. 4.3 a) and Forchheimer’s equation (Eq. 4.3 b),

\[
-\frac{dP}{dx} = \frac{\mu}{k_1} v_s,
\]

(4.3 a)

\[
-\frac{dP}{dx} = \frac{\mu}{k_1} v_s + \frac{\rho}{k_2} v_s^2
\]

(4.3 b)

where \(-dP/dx\) is the pressure drop along the flow direction, \(\mu\) is the absolute viscosity and \(\rho\) the density of the liquid, and \(v_s\) is the superficial velocity. \(v_s\) is defined as the volumetric flow rate \(Q\) divided by the cross-sectional area \(A\) perpendicular to the fluid flow in the porous medium. The constants \(k_1\) and \(k_2\) are usually known as the Darcian and non-Darcian permeabilities, and have the dimensions of square length and length, respectively.

The two equations differ in the assumption of the behaviour of the fluid transported through the porous medium; specifically its velocity. For low flow rates the inertial effects in Forchheimer’s equation can be ignored, to simplify to Darcy’s law, which only includes the contribution of the viscous forces to the permeability. Darcy’s law is applicable at laminar flow which occurs at low flow rates, as opposed to turbulent flow at high flow rates. The
type of flow regime can be estimated with the dimensionless Reynold’s number ($Re$). Darcy’s law is considered valid for $1 < Re < 10$. Outside the laminar flow regime adaptations of Ergun’s equation, originally empirically derived for fluid flow through packed columns, have been proposed to estimate the permeability. The Katz-Thompson model,

$$\kappa = \frac{C \cdot \phi \cdot l^2}{\tau},$$

is a model derived from Darcy’s law and is commonly used to estimate permeability. The model requires information on the porosity ($\phi$), the critical pore diameter ($l_c$), the tortuosity ($\tau$) and a constant $C$, which depends on the distribution of pore sizes in the material. The critical pore diameter, which corresponds to the diameter of the smallest constriction of a set of pores that percolate through the porous structure, can be obtained from the inflection point of a mercury intrusion curve. The tortuosity of the porous material is an important factor in the Katz-Thompson model. Tortuosity can be described as the deviation of a path through connected pores from a geodesic (shortest path through space). It can be calculated from the ratio between the effective resistance of electrical current across the pore phase filled with fluid to the conductance of the fluid itself.

### 4.3.3 Routes to alter the permeability of macroporous ceramics

Each processing method for creating macroporous ceramics with open and interconnected porosity leaves its unique signature on the combination of pore phase parameters. The processing method thus strongly influences the final permeability. The (Darcian) permeability of ceramic particulate filters for diesel flue gases ranges from about $10^{-12}$ m$^2$ for honeycomb dead-end filters, to $10^{-9}$ m$^2$ for fibre or foam filters. Partially sintered powder structures, ceramic fibrous media and honeycombs are commonly employed in filtration processes of liquid or gaseous suspensions. Partially sintered particulate materials are easily produced and commonly display a narrow pore size distribution of which the pore size is mainly controlled by the particle size. For filtering applications, these materials usually display a porosity of 40-50% and pore sizes of 10 µm. Materials with high porosity, up to 90%, but with a wide pore size distribution, can be produced from partially sintered ceramic fibres.

Honeycombs, produced by extrusion or pressing, typically display a highly ordered arrangement of parallel channels with a well-defined shape and size. The cell shape (circular, square, triangular and hexagonal), cell density (4-244 cells/cm$^2$) as well as wall thickness (0.2-1.5 mm) control the
percentage of the open frontal area (30\% to >90\%).\textsuperscript{18,133} The cell wall in honeycomb structures commonly contains pores with mean sizes of 4-50 µm and porosities of 30-50\%.\textsuperscript{133} Ceramic honeycombs used as particulate traps are often referred to as dead-end filters since half of the channels are closed at the upstream end and the other half are closed at the downstream end to capture particles from e.g. diesel-engine exhaust gases.\textsuperscript{10,134}

Reticulated ceramics consist of interconnected pores surrounded by a web of ceramic material and have a higher pore tortuosity compared to honeycomb materials. A high tortuosity of the pore space is favourable for catalytic and filtration processes as it results in flow patterns with high degree of mixing. Reticulated ceramics used for molten metal filtration typically have permeabilities between $10^1$ m$^2$ and $0.5 \times 10^2$ m$^2$, for materials with mean pore sizes up to 6 mm and with a typical cell window diameter of 0.5-1.0 mm.\textsuperscript{23,135}

Reticulated ceramics can be produced by direct foaming of ceramic suspensions, or by impregnation of a polymer foams with a concentrated ceramic suspension (replica method).\textsuperscript{33,36,136} These ceramic materials display open pore structures with porosities up to over 90\% and permeabilities of $10^{-9}$ m$^2$.\textsuperscript{137} However, it is difficult to alter the connectivity of the pore space with the replica method\textsuperscript{12,37} and direct foaming usually renders materials with small pore throats.\textsuperscript{24,36,37} The permeability in reticulated ceramics depends on the size distribution of the cell windows, or throats; a narrow and small throat size distribution leads to low values of the permeability due to the constrictions between cells which results in a large pressure drop.\textsuperscript{23}

The use of dense or hollow polymer beads as a sacrificial templating material offers significant versatility to control the porosity and pore size distribution.\textsuperscript{26,29} With the expandable polymeric spheres (EPS) we have produced highly porous materials with tunable pore size.\textsuperscript{138,139} However, the control of the connectivity of the porous phase with the original technique, presented in Chapter 4.2 is limited.

4.3.4 Alumina particle coating on expandable microspheres

We modified the surfaces of the EPS by sequential, layer-by-layer, adsorption of charged species (anionic and cationic polyelectrolytes and colloidal alumina). An adsorbed layer of alumina particles on the EPS can form an effective boundary layer of particles around the EPS in the gel-casting suspension. Layer-by-layer is an electrostatically driven self-assembly process where charged species in solution adsorb on oppositely charged surfaces.\textsuperscript{140}

The layer-by-layer adsorption onto the EPS was performed in a neutral pH range, where the weak polyelectrolytes are highly dissociated. Fig. 4.13 shows that the cationic polyelectrolyte poly(ethylene imine), abbreviated PEI, which is well known to adsorb strongly,\textsuperscript{141} resulted in a significant
positive charge on the EPS. Several layers of the anionic poly(acrylic acid), abbreviated PAA, and the cationic poly(allylamine hydrochloride), abbreviated PAH, were sequentially added onto the PEI-coated EPS.

Fig. 4.13 shows that the sign of the zeta potential changed with each addition; the addition of PAA produced a negative surface charge and the addition of PAH produced a positive surface charge. The switch in the sign of the surface charge is characteristic for the layer-by-layer process and shows that the most recently adsorbed polyelectrolyte dominates the surface charge.\textsuperscript{142} Positively charged alumina particles (at pH 5) were adsorbed onto the EPS surfaces that had been coated with four polyelectrolyte layers, having an outermost PAA coating with a strongly negative surface charge (Fig. 4.13). The layer-by-layer coating was finished off with a final layer of PAA adsorbed onto the alumina particles to increase the compatibility of the coated EPS with the concentrated alumina suspension containing monomers and cross-linkers in solution.

![Fig. 4.13. The zeta potential of the expandable polymeric spheres (EPS) after sequential adsorption of polyelectrolytes and alumina (Al\textsubscript{2}O\textsubscript{3}) particles. The polyelectrolytes used were poly(ethylene imine) (PEI), poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA). The mean value and the standard deviation of the zeta potential are indicated for each polyelectrolyte addition together with the pH value for the adsorption.](image)

The SEM images in Figs. 4.14(a) and 4.14(b) show that the alumina particles formed a dense layer on the surface of the EPS. The EPS are filled with a blowing agent that expands when heated and thermo-mechanical analysis on the un-coated and particle-coated EPS (PCEPS) showed that the particle coating acted as a crust around the spheres and shifted the temperature induced expansion of the EPS from 88 °C to 98 °C (Fig. 4.14(c)). The
particle-coated EPS had also expanded less than the un-coated EPS when the expansion was complete.

Fig. 4.14. Scanning electron microscopy images of an alumina particle-coated expandable polymeric sphere (PCEPS) in (a) and a close-up of the surface morphology of the PCEPS in (b). (c) shows thermo-mechanical analysis on the un-coated EPS and particle-coated EPS (PCEPS) for the on-set temperature of expansion.

4.3.5 Pore connectivity and critical pore throat control

The macroporous alumina materials were cast into cylindrical moulds, using the EPS, both un-coated and particle-coated (PC), as a templating material, which was burned out before pre-sintering. The moulds restricted the expansion of the EPS in the (horizontal) xy-plane, but left them free to expand in the (vertical) z-direction. Table 4.1 shows how the porosity of the macroporous alumina materials, as determined by X-ray µ-CT, varied with the amount of added EPS. As a result of the alumina particle layer, which restricted the expansion of the spheres, it was necessary to add a higher amount of particle-coated EPS compared to the amount of un-coated EPS to reach similar porosity levels in the macroporous alumina materials.

Fig. 4.15 shows SEM images of MA-EPS-51 and MA-PCEPS-48 adjacent to the corresponding 2D slices from the X-ray µ-CT data, respectively. We identified these specific 2D slices from the xy-plane of the
segmented the data by applying an aligning algorithm to the 3D data-set. The images of the macroporous alumina (MA) in Fig. 4.15 show the difference in pore sizes in the xy-plane between materials templated with un-coated EPS (MA-EPS-51) and particle-coated EPS (MA-PCEPS-48). As a result of the alumina particle layer, which restricted the expansion of the particle-coated spheres, MA-PCEPS-48 showed a higher number of pores with smaller pore sizes compared to MA-EPS-51.

Table 4.1. Porosity derived with X-ray micro-computed tomography of macroporous alumina (MA) materials templated with un-coated expandable polymeric spheres (EPS) or alumina particle-coated EPS (PCEPS).

<table>
<thead>
<tr>
<th>Material label</th>
<th>Amount added of EPS [wt% dwb]</th>
<th>Porosity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA-EPS-76</td>
<td>1.8</td>
<td>76</td>
</tr>
<tr>
<td>MA-EPS-57</td>
<td>1.1</td>
<td>57</td>
</tr>
<tr>
<td>MA-EPS-51</td>
<td>0.7</td>
<td>51</td>
</tr>
<tr>
<td>MA-EPS-46</td>
<td>0.3</td>
<td>46</td>
</tr>
<tr>
<td>MA-PCEPS-67</td>
<td>4.5</td>
<td>67</td>
</tr>
<tr>
<td>MA-PCEPS-48</td>
<td>2.4</td>
<td>48</td>
</tr>
</tbody>
</table>

a The number at the end of each material label refers to the level of porosity in the material.
b The amount of sacrificial templating material, without alumina particle coating, in the gel-casting suspension in wt% dry weight basis (dwb).

Fig. 4.15. Scanning electron microscopy (SEM) images and corresponding two-dimensional slices retrieved from the three-dimensional X-ray micro-computed tomography data for macroporous alumina (MA). The SEM images (a, c) are compared with segmented representations (b, d) with the pores in black and the solid in white. The macroporous alumina materials MA-EPS-51 and MA-PCEPS-48 were templated with un-coated and particle-coated expandable polymeric spheres (EPS and PCEPS), respectively.

The X-ray μ-CT data in Fig. 4.16(b) show that particle-coated EPS created a narrower pore size distribution compared to un-coated EPS in macroporous alumina materials. Fig. 4.16 shows the pore volume distribution of the materials MA-EPS-76 and MA-PCEPS-67 together with representative slices from the 3D data where each pore has been individually coloured.
Fig. 4.16. The pore volume distribution and representative two-dimensional slices, with each pore individually coloured, from the X-ray micro-computed tomography data. The macroporous alumina (MA) material MA-EPS-76 in (a) was templated with un-coated expandable polymeric spheres (EPS), and MA-PCEPS-67 in (b) with alumina particle-coated EPS (PCEPS).

Templating with PCEPS resulted in an increase in the fraction of isolated pore clusters compared to templating with EPS (Fig. 4.17). The particle coating on the EPS not only reduced the expansion of the EPS but also introduced a barrier of alumina particles to separate the pores in the pre-sintered alumina. Fig. 4.17 also shows that the fraction of isolated clusters decreased as a function of increasing total porosity for all the macroporous alumina materials.

Fig. 4.17. The fraction of isolated pore clusters plotted as a function of the total porosity (%) for macroporous alumina (MA). The materials were produced using un-coated or particle-coated (PC) expandable polymeric spheres (EPS) as sacrificial templates.
The mercury porosimetry data in Fig. 4.18 quantify the size of the cell windows, i.e. the throats, over several orders of magnitude. The throats below 1 µm in size are due to interstices between alumina particles, while the larger throats of size 1 to 300 µm are caused by the sacrificial templating material.

The particle-coated EPS resulted in relatively small throats. The low porosity material MA-PCEPS-48 had a majority of throat diameters below 20 µm, while the high porosity material MA-PCEPS-67 displayed throats up to 240 µm. The un-coated EPS resulted in 30-300 µm sized throats in the low porosity material MA-EPS-46 and 8-260 µm sized throats in the high porosity material MA-EPS-76. The presence of smaller throats in the MA-PCEPS materials compared to the MA-EPS suggests that the particle coating forms a crust around the spheres that reduces the coalescence of the EPS when they expand.

Fig. 4.18. Throat size distributions of macroporous alumina (MA) determined by mercury porosimetry. MA-EPS-76 and MA-EPS-46 were templated with un-coated expandable polymeric spheres (EPS) and MA-PCEPS-67 and MA-PCEPS-48 were templated with particle-coated EPS (PCEPS).

A third measure to indicate how well the pore space is connected, apart from the fraction of isolated pore clusters and throat size distribution, is the number of pores that each pore is connected to. The distribution of the number of connected pore neighbours is plotted as their relative frequency of occurrence in Fig. 4.19. The distribution gets narrower with decreasing average porosity in the macroporous alumina. MA-PCEPS-48 stands out with a small and narrow distribution of the number of connected pore neighbours.
4.3.6 Permeability to fluid flow

The differences in local flow paths of fluid permeating the macroporous alumina materials templated with un-coated EPS and particle-coated EPS are visualised three-dimensionally in Fig. 4.20. The two macroporous EPS and PCEPS-templated alumina materials in Fig. 4.20 have similar porosities (46% and 48%, respectively) but quite different velocity and flow fields: in MA-EPS-46 (Fig. 4.20(a)) the fluid mainly permeated through wide passages, whereas in MA-PCEPS-48 (Fig. 4.20(b)) the fluid flow was constricted by narrow pathways between spherically shaped pores. The velocity fields represent the dominating flow in the x-direction and were derived from the calculated permeability.

Fig. 4.21 shows the permeability to fluid flow in the x- and z-directions calculated on sub-volumes from the sacrificially-templated macroporous alumina. The difference in permeability in the two different directions is probably related to the features of the production process: the suspension was cast into cylindrical moulds which restricted the expansion in the xy-plane, but allowed expansion in the z-direction. Fig. 4.21 shows that the permeability of the macroporous alumina increased with increasing porosity. Permeability values were lower for the materials templated with PCEPS compared to the materials templated with un-coated EPS.
Fig. 4.20. Three-dimensional visualisations showing snapshots of the velocity intensities and local flow paths in macroporous alumina materials. The flow paths, advancing in the vertical direction were derived from simulations of permeability. The darker colour (red) represents a high flow velocity. The volumes correspond to 1.44 mm$^3$ of macroporous alumina materials templated with un-coated expandable polymeric spheres (EPS) or particle-coated EPS (PCEPS): MA-EPS-46 in (a) and MA-PCEPS-48 (b).

Fig. 4.21. Simulated permeability plotted as a function of connected porosity for sub-volumes of macroporous alumina (MA) templated with un-coated expandable polymeric spheres (EPS) or particle-coated EPS (PCEPS).

We have also compared the predicted values for the permeability from the Katz-Thompson model (Eq. 4.3 c) with the simulated permeability (Fig. 4.22) for macroporous alumina templated with un-coated EPS and particle-coated EPS, respectively. The permeability was simulated in all directions (x, y and z) using sample volumes (1.44$^3$ mm$^3$) 8 times larger than the volumes used for simulation in Fig. 4.21 to reduce the scatter. Although the value of the constant C in the Katz-Thompson model varies slowly over
a wide range of pore shapes and pore size distributions we used \( C = 0.04 \) corresponding to previous studies.\textsuperscript{70,71} We calculated the tortuosity for each sub-volume and for every direction (x, y and z),\textsuperscript{71} and the critical pore throat diameter was derived from the inflection point of a mercury intrusion curve simulated on each sub-volume.\textsuperscript{124} We found that values calculated with the Katz-Thompson model were in good agreement with the simulated permeability over the investigated permeability range. This agreement confirms that it is the smallest constrictions in a group of connected pores that govern the fluid flow through the macroporous alumina materials.

![Graph](image)

Fig. 4.22. Comparison of the simulated permeability to the estimated permeability derived with the Katz-Thompson model for macroporous alumina (MA). The MA materials were templated with un-coated expandable polymeric spheres (EPS) and particle-coated EPS (PCEPS), respectively.

4.4 CO\textsubscript{2}-capture performance of hierarchically porous ceramic materials

4.4.1 Introduction

Hierarchically porous materials for CO\textsubscript{2}-adsorption combine a high surface area with macropore channels for rapid mass transport and low pressure drop.\textsuperscript{65,143} Current technology for shaping of macroscopic adsorbent bodies is commonly based on the use of relatively high amounts of inorganic binders, such as clay. The inert binder increases the mechanical strength of the macroscopic bodies but reduces the volumetric efficiency of the adsorbents.\textsuperscript{17,60}

Two main routes for producing hierarchically porous ceramic components of zeolitic materials can be identified: assembling micro-/mesoporous powders or precursors into components with macropores; and adding micro-
Nucleation and in-situ growth of zeolites on macroporous sacrificial templates, such as polymer foams and biological specimens, result in hierarchically porous materials with a well-defined macropore structure and of high specific strength. However, these methods are associated with long processing times. Macropores can also be introduced in microporous powder bodies by templating, foaming of colloidal suspensions, or by (partial) sintering of powders.

Micro- and mesoporosity can be introduced to macroporous supports by slurry-coating, chemical or physical vapour deposition or by the use of preceramic polymers. An advantage of slurry-coating, compared to in-situ growth of zeolites, is that the deposited coatings are porous which provides higher accessibility to the active adsorption sites.

The aim of the work presented in this chapter was to compare the CO₂-uptake performance of hierarchically porous ceramic materials produced through colloidal processing. Two different types of materials were produced: macroporous alumina supports coated with zeolite 13X; and hierarchically porous silicalite-1 and zeolite 13X monoliths sacrificially templated with glassy carbon spheres or carbon fibres.

4.4.2 CO₂-uptake of macroporous alumina coated with zeolite 13X

The macroporous alumina supports were produced using un-coated expandable polymeric microspheres (EPS) with a mean size (D₅₀) of 33 µm as a sacrificial templating material. The supports were sintered at 1500 °C. The surfaces of the alumina supports were rendered positive by adsorbing PEI before impregnating the support with a suspension of the negatively charged zeolite 13X and kaolin. The coating process of the alumina supports was performed with suspensions of zeolite 13X and kaolin at three different pH values: 7.0, 8.0 and to 9.6, respectively. The amount of zeolite 13X was kept constant (20 wt%) and the kaolin content was varied between 3.0 wt%, 4.0 wt% and 6.5 wt% dry weight basis (dwb) with respect to zeolite 13X, respectively. After drying, the materials were heat treated up to 780 °C.

The SEM images in Figs. 4.23(a) and 4.23(b) show that the alumina pore walls were homogenously coated with zeolite 13X without bare patches, which indicate that the zeolite 13X/kaolin suspensions have penetrated the connected porosity of the alumina monoliths. Fig. 4.23(c) shows that the throats remained open after the coating process. This is essential for the performance as a gas adsorbent where all the coated macropores should be accessible for the flowing gas. The thermal treatment resulted in a particulate film that adhered firmly to the alumina, exemplified in Fig 4.23(d) which shows a dense alumina pore wall coated with tightly packed zeolite 13X.
particles on each side. The alumina supports contained 9-13 wt% of zeolite 13X after the coating process.

The highest specific CO$_2$-uptake, with respect to the amount of zeolite 13X, was recorded for the alumina-zeolite 13X composites where the zeolite 13X suspension had a pH of 9.6 during the coating process (Fig. 4.24(a)). The specific CO$_2$-uptake of alumina supports coated with zeolite 13X decreased as a function of decreasing pH of the suspension, as seen in Fig. 4.24(a). As recently shown by Akhtar et al. the pH of a zeolite 13X suspension has a notable effect on its flow properties, the lowest viscosity of a zeolite 13X suspension was recorded for a pH of 9.6 and the viscosity increased notably below pH 9.6. This suggests that the higher viscosity of the particle suspensions at pH values below 9.6 reduced the ability of the zeolite 13X suspension to efficiently enter the macroporous alumina supports during the coating process.

The results shown in Fig. 4.24(b) suggest that the relative amount of kaolin also has an influence on the specific CO$_2$-uptake. The materials that
contain zeolite 13X coatings with 3.0 wt% kaolin showed a higher specific CO₂-uptake compared to coatings with 4.0 wt% and 6.5 wt% kaolin. The addition of an inert, nonporous binder does not only dilute the active component but there is also a risk that the inorganic binder will reduce the accessibility of the microporous adsorbent and thus reduce the CO₂-uptake.

4.4.3 CO₂-uptake of sacrificially templated zeolite monoliths

Hierarchically porous monoliths of silicalite-1 or zeolite 13X were produced by colloidal processing followed by pressureless thermal treatment to remove the carbon-based sacrificial template. Kaolin was used as a non-zeolitic binder. To ensure homogenous mixing of the templating material in the final materials, the carbon fibres and carbon spheres were coated with zeolite particles through a polyelectrolyte-assisted process before mixing with the colloidal suspensions. The powder mixtures were dried, unis- tatically pressed, and thermally treated to remove the carbon materials. The monoliths were consolidated at an elevated temperature: the silicalite-1 monoliths at 1200-1400 °C; and the zeolite 13X monoliths at 780 °C.

The SEM images in Fig. 4.25 show that after thermal treatment the silicalite-1 monoliths (Figs. 4.25(a) and 4.25(b)) contain large uniform channels with a pore diameter of 8 μm, distributed homogeneously throughout the hierarchically porous material. In addition to the large macroporous channels, the monolith contains inter-particle voids and the inherent micropores characteristic of silicalite-1. Figs. 4.25(c) and 4.25(d) show that the zeolite 13X monoliths also exhibit large channels with a pore diameter of 8 μm, and spherical pores with pore diameter of 40-80 μm. The
channels and spherical pores are imprints of the sacrificial carbons fibres and carbon spheres, respectively.

Fig. 4.25. SEM images of the hierarchically porous monoliths after thermal treatment: (a) silicalite-1 monoliths templated with carbon fibres; (b) silicalite-1 monoliths templated with glassy carbon spheres; (c) 13X zeolite monoliths templated with carbon fibres; and (d) 13X zeolite monoliths templated with glassy carbon spheres.

The CO$_2$-adsorption isotherms of the silicalite-1 monoliths (Fig. 4.26(a)) show that the deagglomeration and the addition of 5 wt% of kaolin binder resulted in a relatively small reduction of the CO$_2$-adsorption capacity; from 2.1 mmol/g for the as-received silicalite-1 powder to 1.85 mmol/g for the monolith. Similar to previous studies,$^{143,152,158}$ we found that the consolidation temperature of the monoliths had a great influence on the adsorption capacity of the zeolite monoliths. The silicalite-1 monoliths thermally consolidated at 1300 °C retained a CO$_2$-adsorption capacity of about 1.7 mmol/g while an increase in the consolidation temperature to 1350 and 1400 °C greatly reduced the CO$_2$-uptake to 0.75 mmol/g and 0.30 mmol/g, respectively. This dramatic reduction in the CO$_2$-uptake is associated with the loss of the crystallinity and collapse of the microporous network of the zeolites at high thermal treatment temperature.$^{159}$ The
strength of the hierarchically porous monoliths is around 1 MPa, which is comparable to previous studies of silicalite-1 monoliths consolidated by pulse current processing.\textsuperscript{152}

Fig. 4.26(b) shows that the CO\textsubscript{2}-uptake of 13X zeolite monoliths consolidated at 780 °C containing 5 wt% of kaolin had a CO\textsubscript{2}-adsorption capacity of up to 6 mmol/g. The CO\textsubscript{2}-adsorption capacity of the 13X monoliths reduced significantly from 6.62 mmol/g for the as-received powder to 2 mmol/g when 45 wt% of kaolin was added (Fig. 4.26(b)). The strength of hierarchically porous monoliths of 13X with only 5 wt% kaolin was between 0.2 to 0.6 MPa, which is comparable to the previously reported binder-less 13X monoliths.\textsuperscript{143}

![Fig. 4.26. CO\textsubscript{2}-adsorption isotherms of (a) silicalite-1 monoliths as a function of consolidation temperature (°C), and (b) of 13X monoliths as a function of the kaolin content (wt%).](image)
5. Summary and conclusions

This thesis explored macroporous alumina materials produced by a novel method which combines gel-casting with expandable polymeric microspheres (EPS) as a sacrificial templating material. We demonstrated how the expansion of these gas-filled EPS can be used to create macropores inside a powder suspension when heated. The on-set of the polymerisation of the gel-suspension was designed to match the thermally induced expansion of the EPS to avoid cracking and warping. The expandable microspheres introduce a relatively low amount of templating material (1-2 wt%) to the powder body, which facilitates a fast and simple removal of the organic constituents. By controlling the amount of the EPS we were able to tune the porosity up to 86% in the cast alumina materials.

The volume expansion of the EPS was also used for direct casting of near-net shaped macroporous bodies of complex shape. The internal pressure that the expanding microspheres create is sufficient to force the suspension to fill a closed mould. Surface topology of varying complexity was replicated with a high degree of fidelity.

The three-dimensional (3D) structure of these macroporous alumina materials was imaged by X-ray micro-computed tomography (µ-CT). We showed that details of the porous and solid phases could be captured in the segmented (binarised) data by comparing a scanning electron microscopy image of a cross-sectional cut of the material with the corresponding cross-section of the segmented 3D data. The macroporous alumina materials were visualised with 3D representations of the segmented data and the corresponding pore-network models.

The open porosity obtained from the X-ray µ-CT was in excellent agreement with the porosity values obtained from mercury porosimetry measurements of pores larger than the X-ray µ-CT resolution (3 µm). According to the X-ray µ-CT data analysis the pore size distribution resulting from using the EPS as a sacrificial template was relatively wide (3-450 µm).

We also showed that the pore and throat size distributions can be quantified by one single extrusion and intrusion cycle with water-based porosimetry. The throats are the openings, or windows, between connected pores. They are important to quantify since they are the constrictions between pores which limit the flow of gas or fluid. Characterisation with water-based porosimetry is relatively simple and a more readily available
option for characterising macroporous ceramics compared to mercury intrusion and X-ray μ-CT.

The size of pore throats and the connectivity of the pore space in the macroporous alumina materials were tuned by modifying the sacrificial templating method. We coated the EPS with ~10 wt% (dry weight basis) alumina particles using layer-by-layer adsorption of polyelectrolytes and alumina particles. The particle coating on the EPS resisted the heat induced expansion of the spheres in the gel-casting suspension, and in the pre-sintered materials this resulted in smaller pores and lower porosities compared to using un-coated EPS.

The particle-coating on the EPS also reduced coalescence of the expanding spheres, which doubled the fraction of pore clusters isolated from the main percolating pore phase when templating with particle-coated EPS vs. un-coated EPS. 3D analysis with X-ray μ-CT showed that the particle coating reduced the dimensions of the cell windows (throats) by 2 orders of magnitude. The particle coating also decreased the number of cell windows (connections) between neighbouring pores.

We simulated the permeability of fluid flow in the macroporous alumina from the 3D data acquired by X-ray μ-CT. The permeability was decreased by up to 2 orders of magnitude when templating with particle-coated EPS compared to un-coated EPS in macroporous alumina materials of similar porosities. The simulated permeability and the permeability estimations from the Katz-Thompson model were in good agreement over the whole range of investigated permeability for all macroporous alumina materials. This agreement confirms that it is the smallest constrictions (smallest throats) in a group of connected pores that govern the fluid flow through the macroporous alumina materials.

The macroporous alumina materials were also used as supports for coatings of zeolite 13X particles: a CO$_2$-adsorbing material. The alumina supports were impregnated with a colloidal suspension of zeolite 13X and kaolin which resulted in a particle coating on the surface of the macropores. Evaluations of the specific CO$_2$-uptake, with respect to zeolite 13X content, showed that the optimal pH for the coating process of the macroporous alumina with a colloidal suspension of zeolite 13X and kaolin was determined to be pH 9.6. The specific CO$_2$-uptake was further optimised by reducing the amount of binder (kaolin) down to 3 wt% for coatings produced at pH 9.6.

Other CO$_2$-absorbing materials studied were hierarchically porous zeolite monoliths of zeolite 13X and silicalite-1. They were produced by colloidal processing and sacrificial templating followed by pressureless thermal consolidation. Carbon fibre and glassy carbon spheres were used as sacrificial templates to produce macroporous monoliths. The appropriate temperature for the consolidation of the silicalite-1 monoliths (containing
5 wt% of kaolin) was optimised to retain a CO$_2$-adsorption capacity similar to the as-received powder.

The zeolite 13X coatings (applied at pH 9.6 and containing 3 wt% of kaolin) in the macroporous alumina supports showed a similar CO$_2$-adsorption capacity as zeolite 13X monoliths (containing 5 wt% kaolin) with the same heat treatment. The hierarchically porous zeolite monoliths had a low strength compared to most ceramic foams and support materials. However, the monoliths showed a significantly higher CO$_2$-uptake, with respect to both volume and weight, compared to the zeolite 13X-coated alumina supports. Compared to previous studies the hierarchically structured CO$_2$-adsorbents contained very low amounts of inactive binder (kaolin) while still being mechanically stable.
6. Outlook

This thesis has demonstrated how micro- and macroporosity can be combined in ceramic bulk materials and how these materials can be used as hierarchically structured adsorbents for CO\textsubscript{2}-separation. Hierarchically structured adsorbents have the potential to increase the efficiency of swing adsorption processes in post-combustion separation of CO\textsubscript{2} compared to packed beds\textsuperscript{42,65,160} It is therefore interesting to develop new, versatile methods to produce hierarchically structured adsorbents. It is also important to better understand, and quantify, how the structure of the macroporous space influences the CO\textsubscript{2}-uptake efficiency.

Sacrificial templating using a woven three-dimensional (3D) mesh in combination with gel-casting a suspension of microporous particles would yield hierarchically porous materials with well-defined macropores. The connectivity and tortuosity of the pore space and the size of the macropores could easily be designed by altering the pattern of the 3D mesh and the type of material used. The 3D mesh could be produced by knitting techniques and composed of polymeric fibres, carbon fibres or cellulose.

Non-woven macroporous fibres made of microporous particles could be produced by electro-spinning using organic binders\textsuperscript{132,161} The organic binder would assist in a stable assembly of micron-sized fibres. Thermal treatment of the fibres and an inorganic binder, e.g. kaolin, would result in hierarchically porous materials with randomly shaped, distributed and oriented macropores.

Simulations of pressure drop and flow fields from 3D data obtained by X-ray micro-computed tomography (\(\mu\)-CT) could be compared with experimental evaluations to establish robust models for the transport properties of the hierarchically porous materials. The knowledge of the topology of the macropore space could be related to the degree of accessibility of the micropore space and the CO\textsubscript{2}-uptake of the hierarchically structured adsorbent as a function of time, flow rate, flow velocities and pressure drop.

Imaging with X-ray \(\mu\)-CT could however be circumvented if the topology of the macroporous space was well defined. With a knitted 3D mesh as a sacrificial template the resulting macroporous space could be directly described by a computer model\textsuperscript{162} The shapes and sizes of the macroporous space could then be verified with more readily available techniques, e.g. imaging with scanning electron microscopy and quantification with water-based porosimetry, as described in this thesis.
7. Populärvetenskaplig sammanfattning


Men vad är egentligen makroporösa keramer och varför är de viktiga?
Keramer är mycket hårdt men spröda material som kan användas vid mycket höga temperaturer och är dessutom resistent mot aggressiva kemikalier. Vi använder keramer i våra dagliga liv: vi äter på tallrikar av porslin och färdas i bilar och bussar med motorer där flera komponenter består av keramer. De makroporösa keramer jag har tillverkat och studerat har håligheter (porer) som är 0,03-0,45 millimeter stora.

Kombinationen av makroporositet och keramers temperaturbeständighet är intressant där det behövs hårdt och lätta material som klarar höga temperaturer. Makroporösa keramer används idag bl.a. som partikelfilter i dieselmotorer, bärare av katalytiskt aktivt material i fordon, för filtrering av smält metall, värmeisoleringsmaterial i ugnar och i biomedicinska sammanhang.

Hur jag ”bakade” makroporösa keramer med mikrosfärer.

Hur ser då det bakade materialet ut inuti?
Figur 4.4 (a) och (c) visar 3D-bilder som jag tagit fram med hjälp av röntgentomografi av de makroporösa keramerna. Figur 4.4 (b) och (d) visar hur porerna i figur 4.4 (a) och (b) hänger ihop med varandra. Porerna representeras av sfärer och en cylinder mellan sfärerna visar att porerna hänger ihop.

Öppningarna mellan porerna kallas fönster och ett exempel på hur ett fönster kan se ut visas i figur 4.10 (c). Det är viktigt att kunna ändra antalet fönster och deras storlek eftersom öppningarna bestämmer hur en vätska (eller gas) flödar genom det keramiska materialet. Om fönstren är små och få till antalet ökar det motståndet för den genomflödande vätskan. För att materialets egenskaper ska vara förutsägbara och det ska bli så användbart som möjligt är det viktigt att kunna skräddarsy porsystemet.

Hur ser det ut när en vätska flödar igenom de makroporösa keramerna?
Jag beräknade (simulerade) hur det skulle se ut när vätska flödar genom de makroporösa keramerna och det visar jag i figur 4.20. I figuren syns bara vätskan och inte det keramiska materialet. Ett material med stora fönster visas i Figur 4.20(a) och ett material med små fönster visas i figur 4.20 (b). Tack vare att jag kan variera fönsterstorleken och antalet så kan jag alltså påverka flödet av en vätska genom de makroporösa keramerna. Jag kunde beräkna flödet av vätska och ta fram de tre-dimensionella bilderna tack vare samarbetet med mina forskarkollegor vid Australian National University i Canberra, Australien.

Makroporösa keramer som bärare av ”koldioxid-dammsugare”.
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Låt oss ge varandra tid,
låt oss göra famnen vid,
låt oss älska, låt oss sjunga,
inte hålla tand för tunga,
låt oss skratta, låt oss leka
låt oss sorgerna beveka,
låt oss jaga tvivlen bort,
livet är så gränslös kort!
- Bo Setterlind
9. References