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**Study and characterization of capillary imbibition through SiC porous matrix
for optimized fabrication of ceramic matrix composite components for gas
turbine engines**

KARTIKEYA UPRETI

Département de génie mécanique

Thèse présentée en vue de l'obtention du diplôme de *Philosophiæ Doctor*
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Cette thèse intitulée :

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turbine engines**

présentée par **Kartikeya UPRETI**

en vue de l'obtention du diplôme de *Philosophiæ Doctor*
a été dûment acceptée par le jury d'examen constitué de :

André GARON, président

Sylvain TURENNE, membre et directeur de recherche

Étienne MARTIN, membre

Philippe CAUSSE, membre externe

DEDICATION

"There is no knowledge for the seekers of comfort, and no comfort for the seekers of knowledge. A seeker of comfort should give up knowledge, and a seeker of knowledge should give up comfort."

Mahabharata, Udyogapavan-40.6

सुखार्थिनः कुतो विद्या नास्ति विद्यार्थिनः सुखम् ।
सुखार्थी वा त्यजेद्विद्यां विद्यार्थी वा त्यजेत्सुखम् ॥

This work is dedicated to everyone who has contributed in every way possible including family, friends, and everyone else associated with the progression of this endeavour and everyone's combined efforts have made it possible for this work to be completed with invaluable enriching experience...

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This accomplished research work has witnessed the cultivation and integration of numerous individual intellect, each of whom has played a pivotal role in the successful completion of this work, notwithstanding the setbacks endured as a result of the pandemic and associated challenges. This work represents the combined results of all the involved individuals with this project in various capacities. Henceforth, the profound appreciation for the confidence and dedication exhibited by the participants who have actively contributed to this scholarly work has been truly remarkable and worth appreciation.

I wish to express my utmost gratitude to all the esteemed members of the jury who have graciously consented to participate in this research work as evaluators who are tasked with necessary positive feedback for further improvements. The principal contributors to this research project has been École Polytechnique de Montréal, whose provision of essential technical resources has facilitated the successful completion of this scholarly investigation that was laboratory intensive. The involvement of Safran Ceramics, the industrial collaborator for this project, has proven to be instrumental in steering the research efforts towards the intended trajectory and minimizing any deviations from the primary scope with regular feedback for continuous improvements, thanks to their consistent provision of technical assistance whenever required. I am profoundly grateful to every individual who has contributed to the fruition of this work, for it is through their invaluable involvement that this undertaking has been brought to its timely completion.

The participating organizations involved in this project have made substantial contributions in terms of proficient resource management and the strategic implementation of technical feedback. The successful completion of this project was achieved through a constructive collaboration between these institutions such as the Natural Science and Engineering Research Council of Canada (NSERC), École Polytechnique de Montreal (EPM), and Safran Ceramics (SCe). Notably, this achievement was made possible due to the provision of necessary financial support. I would like to commence by expressing my profound appreciation to the associated project supervisor at École Polytechnique de Montréal, Prof. Sylvain Turenne, for his invaluable and punctual support in terms of project management and intellectual collaboration, which proved instrumental in attaining the envisioned goals.

This extensive research work has spanned a duration of around four years, during which a multitude of significant occurrences and instances have transpired, fostering the acquisition and cultivation of a diverse array of aptitudes essential for the successful execution of this

research project. These proficiencies extend beyond mere technical expertise, encompassing a broader spectrum of skills. The acquisition of knowledge and experience through solving diverse challenges that manifest as circumstances, encompassing both favourable and unfavourable elements, has played a crucial role in fostering a comprehensive cultivation of a scientific disposition, coupled with adept abilities in the intricate realm of aerospace materials that constitute the process and procedures for composites.

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The team of contributors to the project at École Polytechnique de Montréal also included short-term interns (Thibault Lafay, Bertille Belleville) who made valuable contributions to the cultivation of the knowledge repository and gave a necessary helping hand in the completion of some important experimental work and some comprehensive analysis related to some digressing aspects of this characterization protocols. Christian Charles Martel as technician responsible for the laboratory associated with research chair on High performance composites (CCHP) demonstrated a commendable level of cooperation in the strategic formulation and logistical coordination of technical resolutions pertaining to the diverse array of setup and process-related challenges that emerged throughout the duration of the project.

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During the last four years of the duration of this project, which has now come to its conclusion, it has been an enriching experience to be in the company of so many different personalities and to exchange ideas with such a diverse group of intellectuals. However, the foundation of personal development and growth that has been achieved has been achieved due to this level of variety in experience having such a profound effect on personal growth.

RÉSUMÉ

Le procédé de coulée de barbotine (*slurry cast*) revêt une importance considérable dans la fabrication de céramiques liées à haute température, car il offre un temps de production plus rapide sans compromettre l'efficacité des coûts. La caractérisation du comportement des composites à matrice céramique (CMC) et de leurs phases constitutives présente des difficultés en raison des conditions complexes aux températures élevées d'utilisation supérieures à 1200 °C. Pour relever ces défis, l'infiltration capillaire (*melt infiltration*) est utilisée pour combler la porosité résiduelle à l'issue des étapes de coulée en barbotine et de traitement thermique. Le présent projet de recherche sur l'infiltration capillaire de matrices de carbure de silicium (SiC) a été réalisé à l'aide de fluides modèles à température ambiante pour simuler la montée capillaire du silicium liquide à haute température typiquement utilisée pour les CMC réels.

La présente étude est fondée sur la caractérisation de spécimens de matrices de SiC produites par coulée en barbotine possédant différentes caractéristiques en termes de porosité, d'épaisseur, de morphologie complexe avec différentes sections transversales et des caractéristiques microstructurelles hétérogènes. L'objectif de cette étude est d'obtenir une compréhension complète des mécanismes d'infiltration capillaire impliqués dans la montée de fluides modèles dans une matrice de poudre SiC. La première étape de cet effort a été la caractérisation de la structure de la porosité à l'intérieur des matrices SiC compactes simplifiées, qui servent à illustrer les nombreuses singularités observées dans la matrice granulaire de composites SiC/SiC.

Le diamètre des pores a été estimé à l'aide de la porosimétrie par intrusion de mercure, tandis que la détermination de la valeur du diamètre effectif a été obtenue en utilisant des essais d'infiltration capillaire avec le n-hexadécane et en appliquant la méthode Lucas-Washburn. L'étude et la validation de la dynamique fondamentale de l'infiltration capillaire au sein d'une matrice SiC ont été réalisées grâce à l'application de méthodes expérimentales et à la simulation numérique.

Au cours du processus d'infiltration capillaire à l'intérieur de matrices SiC, une interaction complexe de plusieurs forces contribue à la formation du front d'écoulement liquide. Le comportement d'infiltration est influencé par divers facteurs importants, parmi lesquels la taille médiane des pores, la porosité, et la tortuosité du milieu poreux. L'apparition de deux fronts d'écoulement, à savoir le front de surface (SFF) et le front en volume (VFF), se distingue par des vitesses d'avancées différentes. Les vitesses sont affectées par la distribution

de pression capillaire, qui dépend de la configuration du front de flux parabolique distinctif qui émerge à l'intérieur de la matrice.

Ce travail a permis la corrélation de la cinétique d'infiltration à la température ambiante avec l'architecture poreuse. En outre, un outil de modélisation a été utilisé pour mieux comprendre comment la structure poreuse influence la cinétique et les mécanismes d'infiltration. La microscopie et la tomographie aux rayons X ont été utilisées pour caractériser le réseau poral en deux et trois dimensions. Cette étude comprend également l'établissement d'une nouvelle méthode expérimentale, par essais interrompus, qui facilite l'étude des mécanismes d'infiltration capillaire dans une matrice SiC à l'aide de la tomographie par rayons X.

Mots clés : Composites à matrice céramique (CMC), Coulée en barbotine, Infiltration capillaire, Caractérisation des milieux poreux

ABSTRACT

The slurry cast process holds considerable significance in the fabrication of reaction-bonded ceramic composites under extremely high temperatures, since it provides a faster production time without compromising cost-efficiency. The characterisation of the behavior of ceramic matrix composites (CMC) and their constituent phases presents challenges due to the complex conditions of use at high temperatures over 1200 °C. In order to address these challenges, the melt infiltration (MI) process is used to fill the residual pores after slurry cast and heat treatment processing steps. The present investigation on the capillary imbibition of silicon carbide (SiC) matrix has been carried out with model fluid at room temperature to simulate the behavior of liquid silicon at high temperature in the actual MI process.

The present investigation is based on the characterization of slurry cast SiC matrix specimens demonstrating variations in porosity, thickness, intricate morphology with various cross-sectional profiles, and heterogeneous microstructural features. The objective of this study is to gain a comprehensive understanding of the capillary infiltration mechanisms involved in the ascent of model fluids within a SiC powder matrix. The first step of this endeavour was the characterization of the pore structure inside simplified porous SiC matrices, which serve as representations of the many typical singularities seen in the SiC/SiC composite granular matrix.

The pore size diameter was estimated by the utilization of mercury intrusion porosimetry, while the determination of the effective diameter was achieved by employing capillary-induced infiltration with n-hexadecane and applying the Lucas-Washburn method. The investigation and validation of the fundamental dynamics of capillary imbibition within SiC matrix specimens are accomplished through the application of experimental, optical, and numerical simulation methodologies.

During the capillary imbibition process within the SiC matrix, a complex interplay of several forces contributes to the formation of the fluid flow front. The imbibition dynamics is influenced by various significant factors, among which the median pore size, the porosity level and the tortuosity of the porous media. The occurrence of dual flow fronts, namely the surface flow front (SFF) and the volume flow front (VFF), is distinguished by different rates of advancement. The velocities are impacted by the adverse capillary pressure, which is contingent upon the configuration of the distinctive parabolic flow front that emerges within the matrix.

This work enabled the correlation of capillary infiltration kinetics at ambient temperature

with the porous media characteristics. Furthermore, a modelling tool was used in order to gain a better understanding of how the porous structure influenced the kinetics and mechanisms of infiltration. Microscopy and X-ray tomography have been employed for the purpose of characterizing the poral network in both two and three dimensions. This study also encompasses the establishment of a novel experimental approach by interrupted tests that facilitates the study of capillary infiltration mechanisms in a SiC matrix by the utilization of X-ray tomography.

Keywords : Ceramics matrix composites (CMCs), Melt infiltration (MI), Slurry cast (SC), Capillary imbibition, Porous media characterization

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LIST OF SYMBOLS AND ACRONYMS

<i>HM</i>	High Modulus
<i>UHM</i>	Ultra high modulus
<i>MTS</i>	Methyl trichloro silane
<i>EBC</i>	Environmental barrier coating
<i>MI</i>	Melt infiltration
<i>SC</i>	Slurry cast
<i>RMI</i>	Reactive melt infiltration
<i>CVI</i>	Chemical vapour infiltration
<i>PIP</i>	Polymer infiltration and pyrolysis
<i>LPI</i>	Liquid polymer infiltration
<i>LSI</i>	Liquid silicon infiltration
<i>UHTCs</i>	Ultra high temperature composites
<i>UHTCMCs</i>	Ultra high temperature composites
<i>RVE</i>	Representative Volume Element
<i>MIP</i>	Mercury intrusion porosimetry
<i>SEM</i>	Scanning electron microscopy
<i>CTE</i>	Coefficient of thermal expansion
<i>CFRP</i>	Carbon fiber reinforced polymer
<i>A</i>	Surface area
<i>q</i>	Volume of fluid passing through a unit area in unit time
<i>k_{sat}</i>	Saturated permeability
<i>k_s</i>	Hydraulic conductivity
<i>k_r</i>	Relative hydraulic conductivity
<i>k_{unsat}</i>	hydraulic conductivity of unsaturated porous media
<i>R_{cap}</i>	Radius of a larger single capillary tube
<i>r_{cap}</i>	Radius of smaller single capillary tube
<i>P_c</i>	Capillary pressure
<i>P_L</i>	Laplace pressure
<i>p_{nw}</i>	Pressure in non-wetting phase
<i>P_{viscousloss}</i>	Pressure due to viscous loss in single capillary tube model
<i>p_w</i>	Pressure in wetting phase

θ	Contact angle
η	Viscosity of liquid
γ	Surface tension
σ	Flexural strength
K_{IC}	Fracture toughness
E	Young's modulus
t	Time
$k_{1,2}$	Radii of curvature in Laplace pressure
Δp	Pressure difference
I	Imbibition parameter
L_{eq}	Equivalent length
S	Spreading parameter
s	Degree of saturation
Ca	Capillary number
Ca_{opt}	Optimum capillary number
m	Mass
h	Height
ε	Porosity
d_{50}	Median pore size diameter
ϵ_{Geo}	Geometrical porosity
ρ_{sample}	Density of sample
ρ_{SiC}	Density of SiC
$\alpha_{ }$	Axial coefficient of thermal expansion
$t_{inertial}$	Inertial time scale
$t_{viscous}$	Viscous time scale
H	Jurins height
H_v	Height at which viscous regime begins
w_{avg}	Average thickness
ρ	Density

CHAPTER 1 INTRODUCTION

There is an ever increasing demand for the development of cutting-edge high performance structural materials that have elevated levels of both strength and durability at high temperatures and degrading environments with considerably lighter weight. This is essential in order to meet the growing demands and overcome the obstacles that are present in a variety of important strategic domains in the twenty-first century, including construction, transportation, and energy applications. Because of their remarkable physical and mechanical properties, ceramic matrix composites, also known as CMCs, are currently being contemplated as potentially most suitable choices for high temperature operations in extreme environments (ultra high temperature, corrosion, oxidation, surface erosion).

Ceramic matrix composites (CMC) are the type of material that may be identified by the presence of a second phase that is encased inside a ceramic matrix. Ceramic materials have a number of desired properties, including great strength and hardness, as well as resilience at high temperatures. In addition, these materials may be developed to display certain features such as hardness, self-healing capabilities, or functional attributes such as the ability to perform specified functions. The nature of the reinforcing phase, that is a part of the ceramic structure, is what decides the particular qualities that the material possesses [1].

Growing interest has been shown in the creation of ultra-high temperature ceramics (UHTCs), which could eventually be used in extreme environments. UHTCs have the potential to withstand the harsh aero-thermo-chemical environments of hot zones of gas turbine engines. However, despite the fact that research into UHTCs for this application is still ongoing, the interest in ultra-high temperature ceramic matrix composites (UHTCMCs) has increased over the past ten years [2].

These new generation of lightweight high strength materials have shown their usefulness across a variety of different sectors thanks to the specific properties that they possess. Tools for cutting, dental prosthesis, thermal barrier coatings, and structural materials for the nuclear, energy, military, aerospace, and building industries are some examples of the uses for this material. CMCs offer high specific strength in excess of 900°C as shown in Figure 1.1 when compared to other aerospace grade materials.

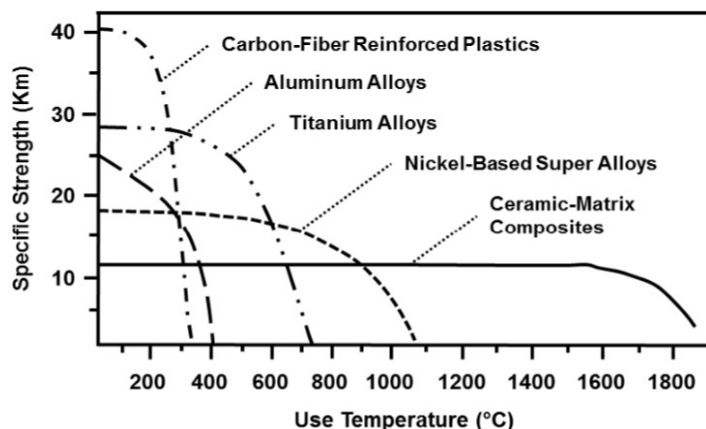


Figure 1.1 Shows the comparison of high temperature operability of CMCs with other materials used in the industry with corresponding strength to weight ratio (Specific strength) [3].

All of the advantageous characteristics of single-phase ceramics are exploited in composites formed of granular matrix reinforced by ceramic fibers [4]. These characteristics include high mechanical strength, resistance to oxidation, and effective radiation shielding. Among the several alternative possibilities, SiC/SiC composites are still regarded to be relatively new class of structural materials. At this point, the majority of their work is concentrated on the developing stages.

It is standard practice for SiC-based composites to apply an interphase layer to the surfaces of the reinforcing fibres in the composite material which is followed by the procedure that involves a fabrication technique for infiltration of ceramic matrix. The aim of this interface is to give protection against aggressive environment conditions at high temperature. In addition, the interphase creates a link that is not very strong at the interface between the matrix materials and the fibres that make up the material. The existence of weak intermolecular interactions makes it easier for the fibres to dissipate the energy related to crack propagation, which in turn prevents the formation of brittle fractures.

Infiltration methods are often utilized during the manufacturing process of ceramic matrix composites to produce the matrix phase in the fiber preform. Within the scope of these manufacturing techniques, the ceramic matrix is created by injecting a fluid substance – whether gaseous or liquid – into the complicated three dimensional fibre structure (slurry cast process, SC), which may either be woven or non-woven in its natural state. This process causes the matrix to take on its final form.

In order to eliminate most of the detrimental porosity in CMC after the slurry cast process, the melt infiltration (MI) with molten silicon is facilitated by capillary forces, which provide a

negative pressure that enables the fluid to occupy the remaining spaces during the last phase of densification. Due to the occurrence of capillary infiltration at elevated temperatures, the characterization of capillary imbibition within a porous SiC matrix poses difficulties. Consequently, it is necessary to investigate a methodology for characterizing the imbibition process induced by capillary action under ambient conditions. This exploration is crucial for the advancement of process optimizations in more accessible environments.

The objective of this thesis was to investigate the influence of various singularities within the granular matrix of SiC, namely at the interface with the fibrous preform, on the mechanisms governing capillary rise. This study thus focuses on the strictly physical aspect of capillary flow, selecting non-reactive fluids. The characterization of industrial composites was conducted both prior to and following melt infiltration, with the aim of formulating hypotheses to elucidate the phenomenon of partial filling in SiC/SiC composites.

Following this, a selection of model materials was made in order to validate these assumptions. The aforementioned materials refer to silicon carbide (SiC) powder compacts, which have been created using the slurry cast (SC) method. These compacts would serve as the matrix material in a SiC/SiC composite. The materials selected exhibit the most accurate replication of the geometric irregularities found in the granular matrix of the composite material, which can have an effect on the filling process. These irregularities include variations in porosity, diameters of pores, gradients in compactness, as well as the existence of cracks and macro pores.

This work focuses on the impregnation of the SiC matrix materials by model fluids at ambient temperature. The objective is to eliminate the inherent reactivity observed during the high-temperature MI process and solely investigate the physical processes associated with capillary rise.

This research work has been presented as a compilation of seven chapters that encompass the evolution of this work. The first chapter includes an introduction to the concept and the definition of the research scope.

The second chapter of this work provides an in-depth exploration of the backdrop that led to its beginning. It begins with a comprehensive overview of several forms of CMC, their respective uses, and an explanation of the fabrication step that is specifically relevant to the scope of this study. This chapter examines the fundamental concepts behind capillary imbibition phenomena.

Chapter three provides an overview of the research and outlines the research objectives. Additionally, it discusses the rationale and background behind the relationship between room

temperature and high temperature capillary imbibition. The general objective may be further categorized into specific objectives to contribute to the overarching global purpose of characterizing capillary imbibition in SiC matrix.

The fourth chapter of this thesis outlines the experimental approach, which begins by proposing a plan of experiments separated into different phases according to their morphological criteria. The manufacturing technique has been succinctly outlined, taking into account the requisite constraints. In addition, the preliminary characterization strategy of capillary rise tests is presented, including two distinct ways, one of which involves the utilization of a doped catalyst. The research has also encompassed the depiction of the microstructure visual characteristics in both two and three dimensions. The present study also includes a discussion on the simulation technique, emphasizing the importance of the model in connection to experimental findings.

In Chapter 5, the outcomes are presented and categorized according to the established phases, taking into account variations in microstructure and geometry of porous specimens. The simulation results have been given for each phase to help the understanding of capillary flow phenomena in porous media. Conclusive observations have been provided for each step as well.

Chapter 6 explores the phenomenon of capillary imbibition in heterogeneous porous media, focusing on the outcomes derived from generated differences in distinct phases. The phenomenon of capillary imbibition is influenced by various geometric and morphological variables, which also elucidate the dynamics of imbibition around macro and micro defects in the SiC matrix. The present study elucidates the interpretation of capillary imbibition simulation, focusing on two crucial microstructural characteristics. Additionally, the conclusions drawn from the analysis are presented, along with suggestions for future research endeavours.

CHAPTER 2 LITERATURE REVIEW

2.1 General characteristics of bulk ceramics and composites

Monoliths and ceramic matrix composites (CMCs) are a special class of refractory and composite materials that find innumerable uses in various industries that require higher strength-to-weight ratio with ultra-high temperature operability. They generally provide excellent temperature resistance with considerably elevated wear resistance.

Monoliths are simple uniform blocks made up of randomized parallel channels that can be extruded into various shapes and sizes. Metal or ceramic monolith catalyst substrates can be impregnated or extruded directly into catalytic bodies after being wash coated with a high surface area catalyst support material. The monolithic parts themselves can be manufactured in a variety of sizes and shapes, with typical cross-sectional areas of round or oval for automotive applications and square for stationary emission uses [5].

Ceramic monoliths made of synthetic cordierite are used in automotive applications. Cordierite is a highly anisotropic crystalline phase with high thermal expansion anisotropy, resulting in extrusion orientation and low overall expansion.

Cordierite-based compositions have a unique combination of several critical properties: (a) thermal shock resistance due to a low thermal expansion coefficient; (b) porosity and pore size distribution appropriate for ease of wash coat application and good wash coat adherence; (c) sufficient refractoriness because the melting point exceeds 1450 °C; (d) sufficient strength for survival in an automotive exhaust environment; and (e) compatibility with washcoat and catalysts [6].

The term "composite" refers to a wide range of materials whose properties can be tailored in accordance with end-use applications by skillfully and precisely combining constituent phases. Theoretically, a wide range of composite properties is possible.

Damage-tolerant ceramic matrix composites (CMCs) with good mechanical properties over a wide temperature range are produced by a reliable combination of continuous/discontinuous fibers and matrix. Compared to metals or other common engineering materials, CMCs are much more resistant to high temperatures and harsh oxidation environments. Some typical examples of manufactured components of ceramic materials and composites within the scope of this research work are presented in Figure 2.1.

The choice of matrix and fiber material depends on the final required properties. Their mechanical behavior exhibits several defining characteristics that distinctly set them apart from

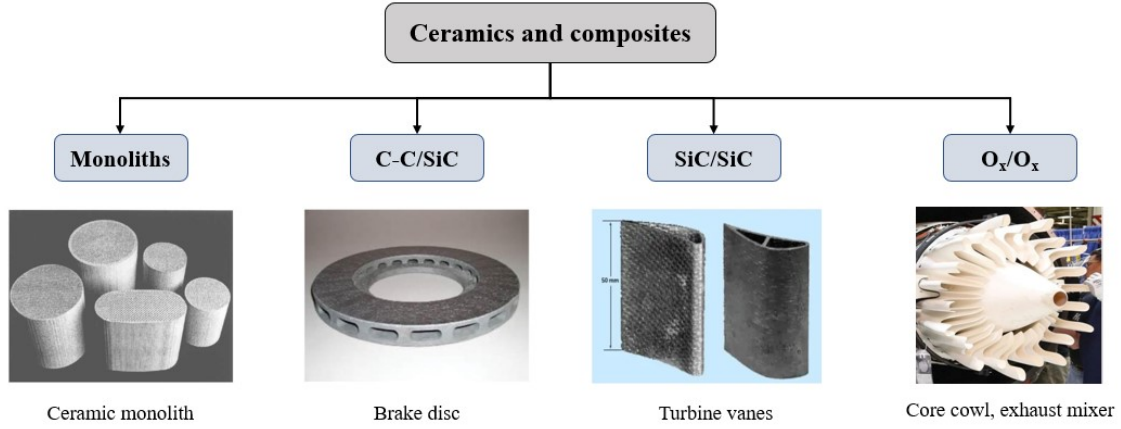


Figure 2.1 Major classification of ceramics and composites with manufactured components [5–8].

homogeneous (monolithic) materials and from other composites such as polymer matrix composites (PMCs) and metal matrix composites (MMCs). These characteristics are influenced by fiber and matrix chemical composition, composite architecture, interphase morphology, and other factors that affect the final thermomechanical properties as enumerated in Table 2.1.

Parameter	Property of CMC
Microstructure	Amorphous with crystalline structure
Mechanical	High strength and modulus
Fracture toughness	Low
Fatigue	Low resistance under fatigue loading
Wear	High wear resistance
Creep resistance	Low
Density	Medium
Operating temperature	Upto 2000 °C

Table 2.1 General characteristics of CMCs that justify the utilization of these materials in regions exposed to ultra-high temperatures [9–11].

While lower elastic moduli help to alleviate some of the stresses that result, weaker materials typically have lower strengths overall. Consequently, these concerns must be taken into account during the design phase of components that will be subjected to thermal gradients and transient loads. There is, however, a lot of room for improvement in every ingredient, so future materials are likely to have enhanced qualities.

2.1.1 Monolith ceramics

The basic mechanical properties of monolithic ceramics are affected by the material grain size, shape and orientation. This grain structure influences directly the toughness, tensile and compressive strengths, hardness, and wear. The elastic and thermal properties do not explicitly depend on the grain size until micro-cracking occurs. The dependence on grain is not ruled out due to the crystal anisotropy of the thermomechanical properties. However, for cubic materials, this dependence is not observed. The general low toughness of monolithic ceramics may be improved by adding reinforcing fibers to obtain a composite material, which offer a considerable increase in the resistance against crack propagation providing increased performance [12].

2.1.2 Carbon/Carbon (C/C) composites

Carbon-fiber-reinforced carbon (C/C) materials were the first to be developed into dependable lightweight structures in high-temperature applications due to their stability at elevated temperature operability and thermal shock resistance, low density, and non-brittle, quasi-ductile fracture behavior. Since the 1960s, C/C materials have been developed for use in the thermal protection systems (TPS) of reusable spacecraft like the US space shuttle and in rocket motor components. The first practical application was brake disks for the Concorde supersonic aircraft [13]. At temperatures above 400 °C, C/C materials are not very stable against oxidation. So, the amount of time that C/C can be used at high temperatures is limited to exposure to oxidative environment. This means that C/C can only be used for short periods of time, like in nozzles for space propulsion, or in non-oxidative environments, like parts in high-temperature furnaces that work in inert gas atmospheres.

Graphitized C fibers, such as high modulus (HM) or ultra-high modulus (UHM) fibers, and highly graphitized C matrices, obtained by thermal treatment of pitch or chemical vapor infiltration (CVI) derived C matrices at high temperatures, are used to address this main drawback of C/C materials and to improve the oxidation stability. Further, salts are infused into C/C materials to act as oxidation inhibitors for short-term use up to about 900 °C. External coatings with oxidation protection layers, such as pure SiC or in combination with a SiO₂ sealing layer or SiC/B₄C/SiC multilayers, applied via chemical vapor infiltration/deposition (CVI/CVD), pack cementation, or slurry coating, could also be significant in improving the useful life of the component [14].

2.1.3 Silicon carbide (SiC/SiC) composites

In a number of cutting-edge applications, lightweight, reusable structural materials are required to function for extended periods of time in extreme high-temperature environments, and silicon carbide (SiC) CMCs reinforced by high-performance, small-diameter (10 to 15 μm) polycrystalline SiC fibers are seen as enabling materials. Hot-section components of military and commercial gas turbine engines are now incorporating the first generations of SiC/SiC CMCs with the thermo-structural capability of operation exceeding 1250 °C [15].

These CMC components not only exhibit significant advantages in terms of reduced engine weight but also in terms of component cooling-air requirements, in comparison to superalloy metallic components, which can only operate at temperatures as high as 1100 °C at best. Since the need for cooling air is highly reduced for CMC components, the engine also benefits from an increased weight-to-thrust ratio, decreased fuel burn, and reduced overall emissions.

2.1.4 Oxide/Oxide (Ox/Ox) composites

Compared to SiC/SiC CMCs, Oxide/Oxide CMCs (mainly $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$) possess superior environmental stability and oxidation resistance. However, this comes at the expense of slightly diminished mechanical properties. For many uses at high temperatures, the creep resistance of Oxide/Oxide CMCs is the limiting property. Finally, Oxide/Oxide CMCs lack the high thermal conductivity and low thermal expansion of silicon-based ceramics. This results in greater thermal strains for Oxide/Oxide CMCs compared to non-oxide composites [15].

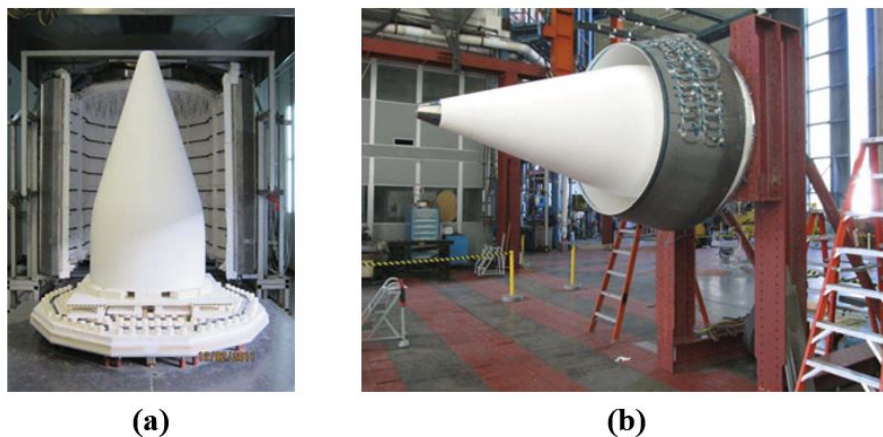


Figure 2.2 Shows the Boeing Ox/Ox CMC acoustic nozzle (a) shows the center-body (b) shows the nozzle assembly for testing [15].

The Ox/Ox CMCs have been intensively explored to minimize the overall cost of production of complicated components for the aerospace sector. Combustor liners are being employed that are Ox/Ox CMC [15]. These classes of CMCs provide a higher temperature operability that promotes more efficient fuel combustion due to overall reduced weight. This generally reduces emissions, with special attention on NO_x emissions. These have also been employed as acoustic nozzle (Figure 2.2), nozzle flaps for fighter aircraft and exhaust ducts for helicopters since they are lightweight and highly resilient [16].

2.2 Applications of ceramic matrix composites

Among the diverse family of high-performance materials, thermo-structural composites are distinctive where the emergence of carbon/carbon composites as the first thermo-structural composites [15] appeared from 1960s. They combine the great customizability of composites with fiber reinforcement with the structural and refractory qualities of graphite and ceramics. These components are crucial for the further development of industrial sectors and fuel innovation, such as aerospace, defense, nuclear and automotive.

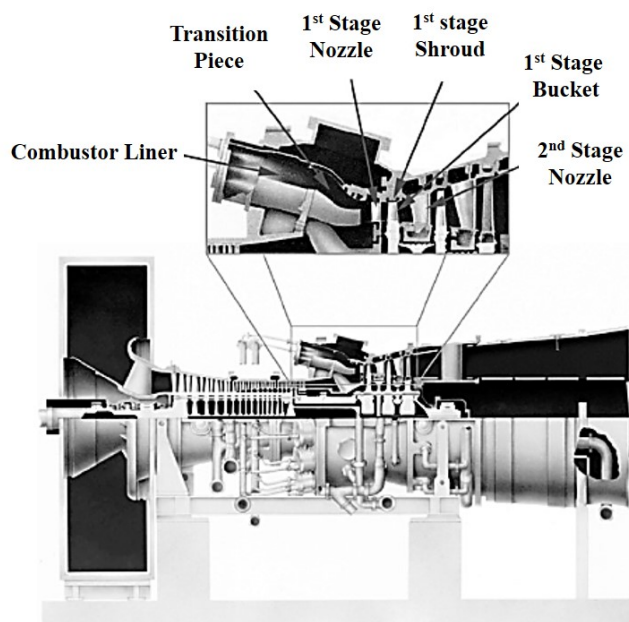


Figure 2.3 Location of different hot gas path components operating under extremely high temperatures of a GE 7FA-class (170 MW) industrial gas turbine engine that are potential candidates for the use of HyPerCompTM composites as a replacement for conventional metal alloy-based materials [17].

The fiber reinforcement and specially designed fiber/matrix bonding eliminate the low fracture toughness of ceramic materials. CMCs are specifically suited to be used in ultra-high

temperature applications due to their low porosity, high toughness, excellent strength-to-weight ratio, low density, creep resistance, and low thermal expansion [17].

In order to satisfy the thermal protection system (TPS) requirements for reusable launch vehicles in the future, CMCs were initially conceived in the 1980s [18]. Due to their inherent qualities (low density, high melting point, excellent mechanical capabilities, and chemical stability), CMCs are ideally suited to replace metallic alloys. These properties are especially targeted for use in extremely hot sections of a gas turbine engine as shown in Figure 2.3.

2.2.1 Carbon/silicon carbide (C/SiC) composites

The range of applications of C/SiC is determined by the combination of temperature, atmosphere, and service time operability. Carbon fibers combined with SiC matrix are very stable at high temperatures, so C/SiC and C/C–SiC materials are capable to be used at temperatures as high as 2700 °C. But their service life is short, mostly because C oxidizes at temperatures above 450 °C and SiC oxidizes actively at temperatures between 1000 °C and 1900 °C, depending on the atmosphere. It could be used to make structures that can withstand high temperatures for short periods of time in rocket propulsion systems. It could also be used to make long-lasting parts like brake discs or satellite structures that work in moderate or low temperatures [19].

CMC has a better potential for usage in lightweight constructions for short-term rocket motor applications. Because they are only used for a short period of time and oxidation is not a major concern. As a result, fiber-based materials can be utilized for high-temperature rocket applications. For thrust vector control (TVC), C/C–SiC jet vanes and sealing ring have been introduced as shown in Figure 2.4(a). These components are placed in the exhaust jet stream and achieve a maximum temperature of 3100 K (≈ 2827 °C) with extraordinarily high heating rates at the leading edge and a local temperature gradient of up to 200 K/mm [18].

C/C–SiC materials are also employed for the fabrication of geometrically stable components, such as calibrating plates [20] or optical units, due to their extremely low CTE¹. A C/C–SiC telescope tube with customized CTE in the axial direction ($\alpha_{\parallel} = 0 \pm 0.1 \times 10^{-6} \text{ K}^{-1}$) is being used for laser communication terminal (LCT) of the TerraSar-X satellite in Figure 2.4(b), which was launched in 2007. A consistent distance between the main and secondary mirrors may therefore be established in the temperature range of -50 °C to $+70$ °C, ensuring secure data transfer with no transmission losses. C/C–SiC has a lower density and greater fracture toughness than Cerodur², allowing for the near-net form manufacturing of thin-walled,

¹Coefficient of thermal expansion

²A glass ceramic used for low thermal expansion applications such as telescope mirror substrates in monolithic and segmented telescopes.

lightweight structures. Moreover, the fundamental shortcomings of CFRP materials, vacuum out-gassing, and hygroscopic swelling may be eliminated [21].

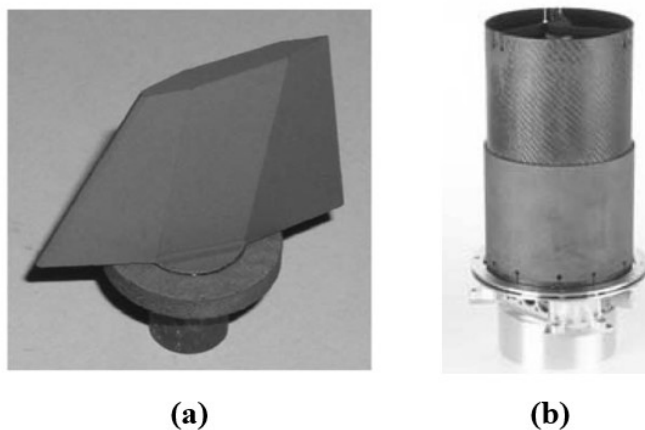


Figure 2.4 (a) C/C–SiC jet vane and sealing ring. (b) C/C–SiC telescopic tube for LCT in the satellite TerraSAR-X (Zeiss Optroniks) [18].

High-performance braking systems, the most common and prospective application field outside of aerospace, have successfully adopted C/C–SiC materials because of their abrasion resistance and excellent friction behavior. C/SiC is utilized for high-accuracy satellite constructions in addition to high-temperature applications. At the moment, C/SiC materials are still only used in small niche markets. For space research and demonstration programs, components are made one at a time or in small groups. In aeronautics, components are made in small series of several hundred per year. In the field of friction materials, brake discs or pads are made in small and medium-sized batches of a few thousand to almost a hundred thousand per year [15].

2.2.2 Silicon carbide (SiC/SiC) composites

Polycrystalline high-strength SiC/SiC CMCs have emerged as a popular hot section material for propulsion engines. There has been a steady rise in high-temperature operability with current advanced SiC/SiC CMC systems that can reach up to 1316 °C (2400 °F) [22]. This limit is poised to be further increased to 1482 °C with the inclusion of advanced SiC fibers and matrix. The applications of CMCs are at present more targeted towards optimum performance at ultra-high temperature (>1200 °C), mainly at the high-temperature zones within a turbine engine. High-temperature zone components have been manufactured gradually by a number of industrial competitors which is shown in Figure 2.5³

³Here (a) and (c) were fabricated as part of AMG (Advanced Material Gas-generator) project and ESPR (Research and Development of Environmentally Compatible Propulsion System for Next-generation Super-

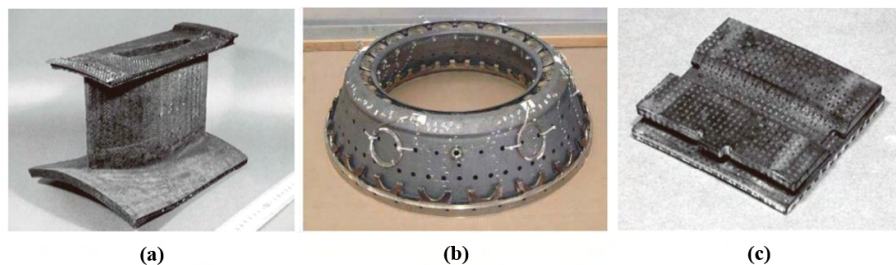


Figure 2.5 (a) SiC/SiC CMC turbine outer ring (b) SiC/SiC combustor liner fabricated by SNECMA and (c) turbine guide vane [23].

Considering the aerospace industry, the incorporation of CMCs can lead to significant improvements in the performance of turbine engines by reducing their weight; this could provide more energy-efficient engine operation including aircraft, helicopters, civilian and military rockets, and re-entry vehicles. Projected skin temperature in future hypersonic aircrafts is expected to be higher than 1600 °C. Other parts, such as radomes, nose tips, leading edges, and control surfaces, will experience only slightly lower temperatures. Currently, one uses sacrificial, non-load-bearing thermal-protection materials on load-bearing components [18].

Low density and higher fracture toughness aid in the manufacture of lightweight, thin-walled structures, even thick-walled systems can be manufactured [18]. MI SiC/SiC are being further developed for special components, including combustion chamber liners, turbine shrouds, and even turbine blades, and have been field tested under actual conditions, resulting in various commercially available MI SiC/SiC materials [24].

Because of their excellent behavior under irradiation conditions, SiC/SiC composites are widely acknowledged to be the most capable of meeting the requirements of nuclear power reactors [25–28]. This result is only provides the highest performance when employing the most recent generation of SiC fibers manufactured by Hi-Nicalon[™] Type-S (HNLS)⁴ and Tyranno[®] SA3 (TSA3)⁵ These fibers are the only ones for which the stability under irradiation has been more or less validated below 1000 °C [31–33].

2.3 Processing of ceramic matrix composites

The majority of elements in the hot zone of a jet engine are thin shells that are a few millimeters thick. As a result, most fiber structures are two-dimensional (2D), such as those formed

sonic Transport) project in the 1990s.

⁴Hi-Nicalon[™] Type S SiC fiber is a multi-filament silicon carbide-type fiber manufactured by NGS Advanced Fibers Co., Ltd. (NGS) of Japan [29].

⁵Tyranno fiber is a continuous ceramic fiber composed of silicon, metal (titanium, zirconium or aluminum), carbon, and oxygen [30].

by simple stacks of woven fiber fabrics or 0/90° unidirectional fiber plies. Nevertheless, because two-dimensional (2D) composites are prone to de-lamination, three-dimensional (3D) self-standing fiber architectures with a small number of fibers woven in the z-direction, perpendicular to the x-y fabric or ply plane, are frequently selected. As a result, in composites with an overall fiber volume fraction of about 45 %, the fiber distribution is generally 20 % along the x and y in-plane axes and a few percent (5%) along the z-axis [34].

The SiC/SiC CMCs processing route includes different steps. The processing flow chart shown on Figure 2.6 presents three major stages: (1) the deposition of the interphase on the fibers (either as received or after some surface treatment to control the interphase bonding to the fibers), (2) the infiltration of the SiC matrix in the fiber architecture or preform, and (3) the silicon melt infiltration. Not shown on the process flow chart, there could be a deposition of an environmental barrier coating (EBC) after the melt infiltration step, such as a SiC seal coating or a multilayered coating, to improve the oxidation resistance of the material. The first stage (production of the interphase) is often accomplished using chemical vapor deposition (CVD) or chemical vapor infiltration (CVI) from a gaseous precursor. The SiC matrix in the second step could be deposited by CVI (gas-phase method) or infiltrated by slurry cast (liquid-phase route) into the fiber preform [34].

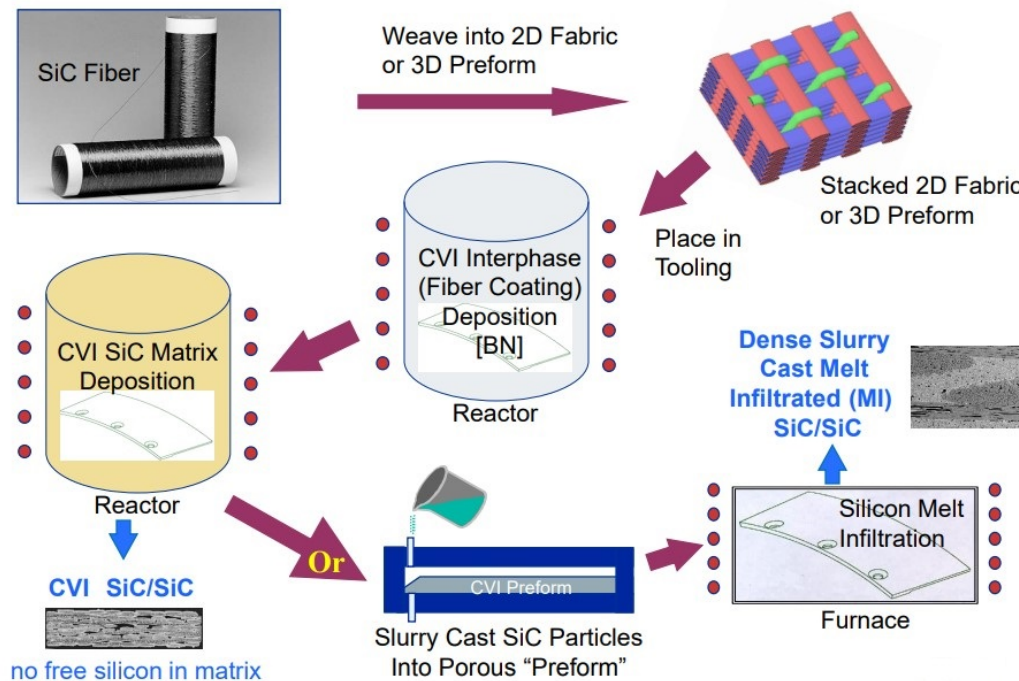


Figure 2.6 Main densification steps for the manufacturing process of CMC SiC/SiC where the final step is melt infiltration [35].

2.3.1 Chemical vapor infiltration (CVI) technique

The CVI process is employed to coat the fibers within the tows with an interfacial coating or interphase, followed by the application of a thin protective SiC matrix layer. Key requirements for interfacial coatings include high environmental durability and high compliance for matrix crack deflection. Those requirements are usually achieved by using an interphase composition based on boron nitride (BN) or pyrocarbon (PyC).

A BN-based interphase coat is applied in the initial step of CVI. Unfortunately, BN coatings can be degraded by contact with molten silicon Si during the melt infiltration process, and consequently, an over-coating of SiC or Si_3N_4 is commonly used to protect the BN layer [17]. Therefore, a SiC overcoat is deposited in the second CVI step to safeguard the BN layer from damage during melt infiltration.

In order to prevent coating degradation during matrix formation and improve component service, the coating thickness could range from 0.1 to 0.5 μm [15] usually varied by a factor of 10 for specific industrial applications. While the interphase and fibers are shielded from further matrix infiltration processes and the environment, the thin CVI SiC matrix coating also provides a highly thermally conductive and creep-resistant matrix constituent.

SiC infiltration follows a procedure that is, for the most part, virtually identical to the coating procedure known as chemical vapor infiltration. Process gas is introduced to the fiber preform (Figure 2.7) while it is being heated in a furnace to temperatures higher than 800 °C (vapor phase). This gas is typically a combination of hydrogen and methyl trichloro silane (MTS or CH_3SiCl_3) where it is used in the process of SiC deposition. The overall chemical reaction of the process is denoted by:



During the vapor infiltration process, gaseous precursor is introduced into the porous fiber preform through the reaction chamber. At the heated surface of the porous fiber preform, the process gas undergoes a chemical reaction that activates the deposition of β -SiC [15]. In this process, a SiC-based matrix is deposited from gaseous reactants to a heated substrate of fibrous preforms of SiC [37].

Pressure, temperature, and the volume ratio of hydrogen and MTS are the three parameters that must be strictly controlled in order to guarantee the deposition of SiC to good and near stoichiometric quality. In the fabrication protocol increasing both temperature and pressure yields a faster deposition rate, which in turn shortens the processing time. The porosity of preform structure influences the CVI process since porosity enables the formation of mi-

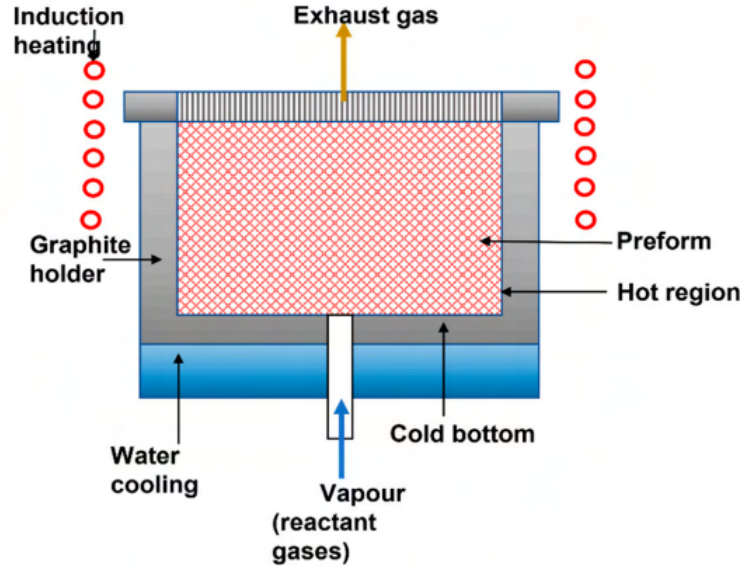


Figure 2.7 Detailed processing schematic of CVI process for the manufacturing of technical CMCs [36].

crochannels that facilitate fluid displacement in the melt infiltration step for densification.

Homogeneous densification requires a trans-laminar open pore system comprising equally distributed, interconnected pores or microchannels with minimum sizes of 10–50 μm . Multi-dimensional fiber architectures and average fiber contents of 40–50 vol.% provide suitable pore structures. Due to microscopic voids that cannot be filled readily, unidirectional or cross-ply laminates based on 1D fiber preforms are crucial for CVI. In the final phase of the CVI process, the porous fiber preform is heated to 800–1100 $^{\circ}\text{C}$ in an infiltration chamber [15].

2.3.2 Slurry cast (SC) process in manufacturing of CMCs

The slurry cast process characterized by the infiltration of a granular matrix suspension to fill the pores of the preform. A mixture of small particles and low viscosity fluid is prepared and is cast at room temperature to fill the pores of the 2D or 3D fiber preform. However, in most cases, the slurry cannot completely penetrate the pores into the tows, due to the closure of the tows resulting from the formation of interphase and CVI coating preceding the slurry cast infiltration. Consequently, some major pores still remain at the end of this consolidation step [15].

As shown in Figure 2.8, the slurry (granular suspension) is introduced into the mold containing the fiber preform under controlled pressure. The slurry fills the pores of the preform and goes through a porous filter at the other face of the preform. The filter allows the liquid

to percolate while retaining consolidated ceramic particles of the slurry in the preform. The resulting particle cake constitutes the ceramic matrix of the composite which is then dried before undergoing the high temperature heat treatment to consolidate the composite. During the drying of the cake, some macropores and cracks may develop in addition to the porosity between the fine particles of the matrix. These micropores and cracks are unavoidable and will be filled by liquid silicon in the following melt infiltration step.

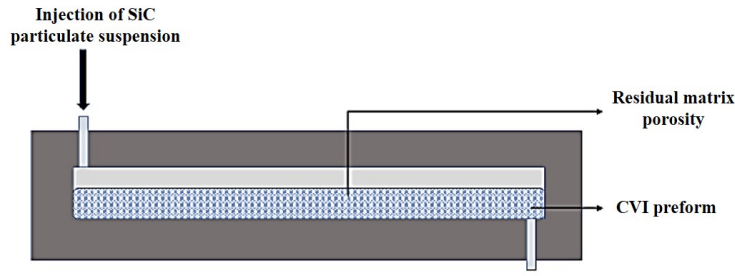


Figure 2.8 Slurry cast process for the filling of fiber performed at room temperature [10].

In this process, the matrix comprises of 23 to 35 vol. % CVI-SiC overcoat with 16 to 18 vol. % SiC particulates [18]. In the slurry cast technique the fibers are held tight by the fiber weave during CVD coating, and hence the bulk of the fibers are in continuous contact with adjacent fibers. Consequently the fibers tend to fail as groups during the fracture failure rather than as individual fibers [38].

The significant drawbacks of this process are longer process times and the presence of residual porosity. However, the advantages outweigh the disadvantages which include a high degree of flexibility in the modification of process parameters such as the deposited material, mass production, and significantly complex components that can be produced. The fiber preforms could have either unidirectional or multi-directional fiber layers depending on the type of weaving used [39]. This processing route step of the slurry cast is succeeded by the melt infiltration (MI) stage which results in further densification of the part with the filling of residual porosity.

2.3.3 Melt infiltration for the densification of CMCs

The melt infiltration (MI) is the final step in the processing route of technical CMCs. This step is crucial because it produces a SiC-based matrix with the least residual porosity, excellent thermal conductivity, and good environmental protection for the CVI-coated fibers. Additionally, it reduces the likelihood of significant matrix failure, increasing the stress levels necessary for the development of damaging through-thickness and delamination cracks in the

composite. In Figure 2.9, the MI processing step is illustrated after producing the matrix of the SiC/SiC composite by CVI/CVD [22].

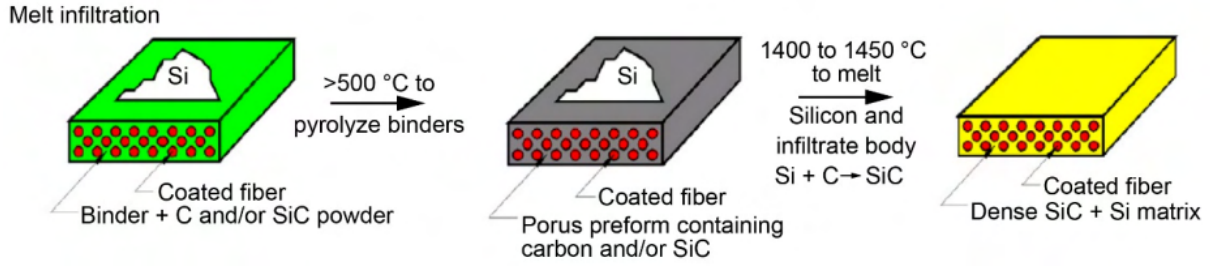


Figure 2.9 Processing stages of melt infiltration (MI) that uses principles of capillarity for filling residual voids [22].

The MI process uses the phenomenon of capillary-induced imbibition (also called wicking) to obtain the densification of a SiC/SiC composite material by the infiltration of liquid silicon. By capillary induced micro and macro flow, the liquid silicon infiltrates the porosity related to the granular SiC matrix and the cracks that are formed during the drying and heat treatment of the consolidated matrix. This capillary imbibition could be carried out under the application of external pressure (inert gas) or under vacuum depending on the end-use specific microstructural requirements.

The fiber-reinforced composite is infiltrated with molten silicon over the melting point of Si (1420 °C) in a vacuum. This results in the imbibition of molten silicon in the porous matrix, in parallel with the chemical reaction between Si and C that forms the compact SiC matrix in reaction melt infiltration (RMI) with reduced porosity. The exothermic chemical transformation by RMI is presented by the equation :



The target is to reduce the amount of free silicon present in the final material [18] because it tends to chemically react and reduce the mechanical properties at high temperatures. When the porous media is made up of only SiC, there is no chemical reaction between the constituent Si and C. This process has the advantage of being a very fast process due to the low viscosity of the fluid, good wettability, and high surface tension that aids in the capillary imbibition. However, due to the application of high temperatures during infiltration, the highly corrosive liquid silicon could lead to significant degradation of the mechanical properties of the fibrous preform during the development of the material by having direct interaction [17].

2.4 Porosity review : morphology and size

Porosity is a significant morphological parameter that is extensively used to characterize the randomized intricate microstructure of certain ceramic based solids. It corresponds to the proportion of void space volume compared to the total apparent volume of a specimen. The porosity may contain entrapped liquid or air. Porosity is observed in many natural and technically made materials so much that it forms part of the basic structure of the void morphology. The porous structure influences a number of mechanical, thermal, electrical, and absorption capacities [40,41].

The ceramic matrix of a composite consists of a randomized pore structure forming an intricate network of micro-channels or micro-pathways that actively contribute to the capillary-induced imbibition at the MI step of the process. Figure 2.10 shows the typical arrangement of pores in granular SiC matrix after slurry cast (SC) but before high temperature heat treatment. Many times during certain fabrication procedure steps, there is marked variation in the anisotropy of the pore shape. Similarly, the sintering process resulting from heat treatment prior to the MI step also has a considerable effect on the final structure of the poral network.

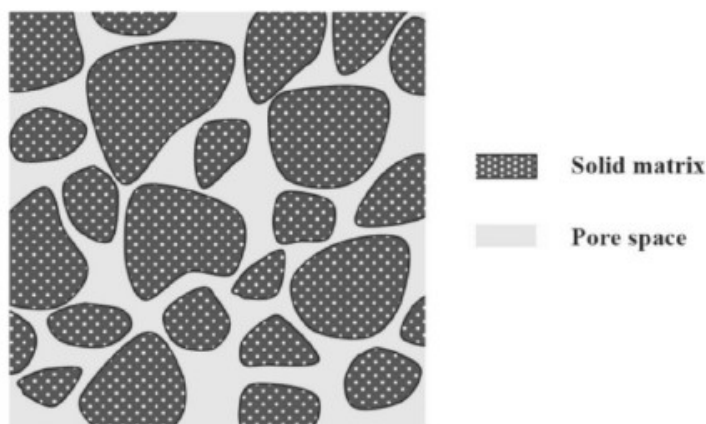


Figure 2.10 Representation of pore space with a matrix with their spatial arrangement [42].

There are various methods to determine porosity, some of which are: optical microscopy, imbibition method, mercury intrusion porosimetry, gas expansion, and density method. The density method relies on the determination of the bulk density of the sample. Since the mass of a porous media depends on the mass of consolidated granular media in the form of the matrix [43], it is important to be able to accurately quantify the precise microstructure of porous material that will be subjected to capillary imbibition at the MI step and its equivalent

at room temperature. It will be shown in the next section that not all pores participate in capillary imbibition.

The geometrical scale of pores in a ceramic matrix varies from micro, meso to macro. Before delving deep into the explanation of the morphology of pores, it is necessary to understand the distinction between granular porous media and consolidated granular porous media along with a distinct and clear classification of the types of pores. The scope of our analysis is limited to consolidated porous networks in a ceramic matrix, which is typical of the microstructure of the composite after heat treatment. The morphology of pores gives rise to different types of porosities based on shape, size, function, and connectivity. This variation in the spatial distribution of pores decides the capillary imbibition dynamics.

2.4.1 Morphology of pores with classification

The classification of pores is mainly based on the role played by the poral network during capillary imbibition process. Some pores actively participate in fluid transmission through their poral network pathways. The connectivity of the pores with their immediate surroundings is an important basis to classify the poral network [40].

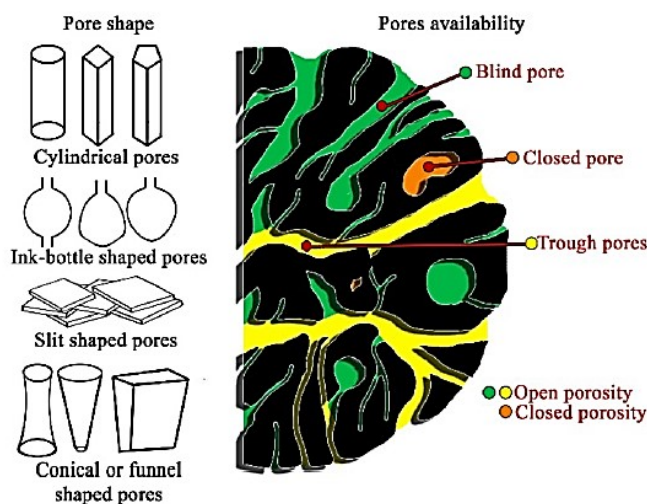


Figure 2.11 Schematic of generic pore classification based on the geometrical shape and availability to contribute to fluid transmission [40].

As one can observe in Figure 2.11, pores communicating with the external surface are classified as open pores. They are accessible for molecules or particulates in the surroundings, while some voids may be open to atmosphere only at one end. They are then described as blind pores. Others may be open at two ends called through pores. The blind, closed and

through pores are classified on the basis of their connectivity with the adjacent pore as a part of a greater representative elementary volume. The through pores are those specific type of pores that contribute to the capillary imbibition of fluid in a porous material.

Closed pores are a product of insufficient evolution of gaseous substances or incomplete filling of the fiber preform during the slurry cast process. Although closed pores do not participate in the capillary flow during MI, they affect the final mechanical properties of solid materials [44].

The pores are also primarily classified based on their pore size, shape, and functions such as micro, meso, and macro based on the scales as tabulated in Table 2.2. To better comprehend the scales of the different classifications, the topological relation with the pore spaces could be discussed with emphasis on its geometrical integrity. With respect to their origin and structure, pores are well categorized into two main divisions. The intra-particle pores that are allocated between individual particles and predominantly are defined as structurally intrinsic pores. In some processes, due to certain reactions, a new set of porous geometry could be created. The newly formed pores are classified as injected intrinsic pores [44].

Types of pores (nm)					
Classification by pore size	Macro-	Meso-	Micro-	Supermicro-	Ultramicro-
Dubinin, 1979	$d > 200 - 400$	$200 - 400 > d > 3 - 3.2$	$d < 0.6-0.7$	$3 - 3.2 < d < 1.2 - 1.4$	-
IUPAC, 1972	$d > 50$	$2 - 50$	$d < 2$	$0.7 - 2$	$d < 0.7$
Cheremskoj, 1985	$d > 2000$	-	$2000 > d > 200$	-	$d < 2 - 4$
Classification by pore function	Transmission	Storage	Residual	Bonding	
Greenland and Pereira, 1977	50,000 - 500,000	500 - 50,000	$d < 500$	$d < 5$	-

Table 2.2 Classification of pores based on the two criteria and their size range for each function (in bold) [40].

Micro pores can contain the smallest molecules of fluid for which the limit to be in the micro-domain would be around 3 nm. They cannot specifically be grouped together with the fluid phase but rather more into the realm of molecular dynamics. At this scale, the properties of fluid such as viscosity and interfacial tension are no longer significant in the flow rheology through these pores. Here the intermolecular forces exerted by the solid wall primarily dictate the behavior of the fluid molecules [42]. These intermolecular forces are a direct result of the inherent cohesion adhesion between the molecules of the designated phases (solid and fluid).

Meso pores have the capacity to include liquid phases. The fluid entrapped in these pores is named by its state of capillary, which is linked to capillary pressure. Interfacial tension also plays a pivotal role in affecting the dynamics in this size domain. The confinement of fluid within meso pores result in the reduction of vapor pressure in comparison to the saturated

vapor phase in the free state [42]. There are various categories of pore sizes described in various literature. Depending on the authors, the scale of meso pores goes from 2 to 400 nm. This scale corresponds to the one that is mostly concerned with capillary phenomena.

Due to the variation in the processing and fabrication, the pore morphological character is very diverse. Porosity usually comprises a dominant porosity type with one or two further secondary porosities. These secondary porosities do not always conform to the dominant porosity type. This diversity in the nature of porosity dispersion depends a lot on the various process parameters.

Therefore, a proper trade-off is desired during the fabrication of a porous matrix. This trade-off would balance (as much as possible) the desired morphology of pores with the desired mechanical properties. Very often, the issue of heterogeneity, pore anisotropy along with anisotropic patterns is neglected. The microcracks, however, are significant in their impact depending on pores, grains, orientation, and shape factors whose combined effects cannot be neglected.

A key factor of CMCs as compared to other materials in similar classes is the nature of failure; it is the brittle matrix that fails first under load. Beyond the proportional limit, the matrix undergoes multiple microcracking under load [18]. A typical SiC/SiC CMC microstructure obtained after slurry cast and Si melt infiltration processes is shown in Figure 2.12. As can be seen in Figure 2.12, the liquid Si (white phase) can migrate in most pores and cracks, small or wide, during melt infiltration (MI).

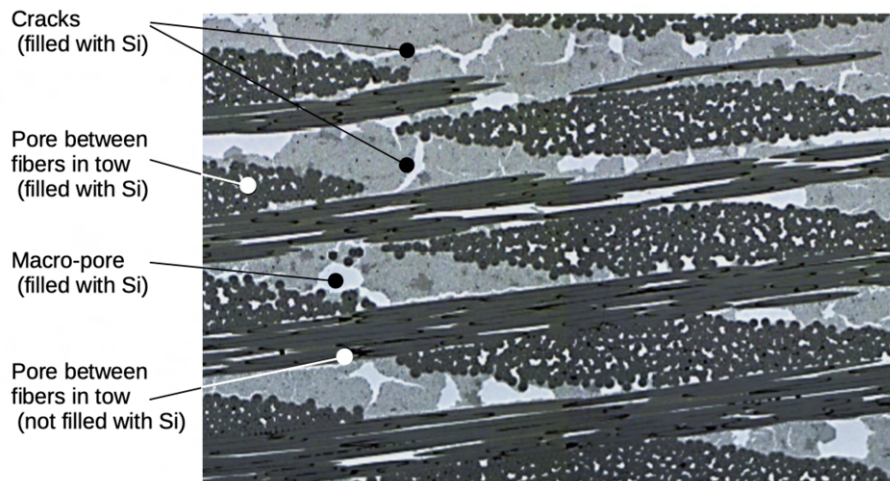


Figure 2.12 Typical microstructure of a SiC/SiC CMC after SC and MI. At this scale, the fine porosity located between Sic particles of the matrix cannot be seen. Black phase: pores; dark grey: fibers; light grey: SiC granular matrix; white: Si after MI. Image provided by Safran, used with permission.

The fine pores between particles of the matrix appear to be completely filled under these conditions. However, certain zones located between fibers into the tows cannot be filled due to the closure caused by CVI coating that could be more or less important. These matrix cracks also run circumferentially around the tows. Larger-sized voids in the matrix form denuded matrix regions that principally occur at the intersection of four orthogonal tows [45]. These initial cracks are generated during the processing of the CMC. They tend to propagate under externally applied load.

The propagation of cracks depends largely upon the fiber orientation that is in contact with the matrix. In the case of cracks perpendicular to the fiber axis, the deflection of cracks gives protection to the fibers. Debonded interfaces are a necessity for crack deviation. The location of debonding is controlled by the strength of the interface and transverse strength (perpendicular to the matrix crack direction) [18].

Porosities generated by matrix cracks are generally of the order of (100-200 μm); the cracks are predominantly circumferential and confined in the plane normal to the axis of adjacent tow. The formation of matrix cracks occurs during the cooling of the composite as a result of tensile strains created in the matrix due to the difference in the linear coefficients of thermal expansion for the matrix and the fiber parallel to its axis. The denuded matrix regions are developed during the CVI process, this happens due to the time required to fill large voids at the intersection of tows [45].

2.4.2 Influence of porosity on properties of composites

Porosity, being one of the fundamental morphological characteristics plays the most dominant role in the final thermomechanical properties of CMCs. The fabrication process and its parameters determine whether the resulting material will have large or restricted porosity, depending on both the fabrication method and the parameters used. Factors such as the size and shape of the components influence the fabrication process used making it a dynamic process. The quantity and character of the porosity intended or permitted in the component is also an essential issue.

When high levels of properties are desired (strength, fracture toughness, hardness, wear, and erosion resistance), it is often necessary to reduce the level of porosity. The porosity usually lowers properties by a lot. However, for some technical reasons, some thermomechanical properties can be improved by controlling adequately the level of porosity. To do this, it is necessary to choose how much and what kind of residual porosity is left over.

Mechanical parameters such as Young's modulus (E), strength (σ), and fracture toughness (K) all dropped as porosity increased (Figure 2.13); however, the loss in strength and tough-

ness was less severe than the change in Young's modulus. Porosity enhanced strain tolerance and fracture energy. The fact that the fracture process is followed by the pullout of the fibrous Si_3N_4 grains and an increase in fracture surface roughness might explain this minor increase in fracture energy [46].

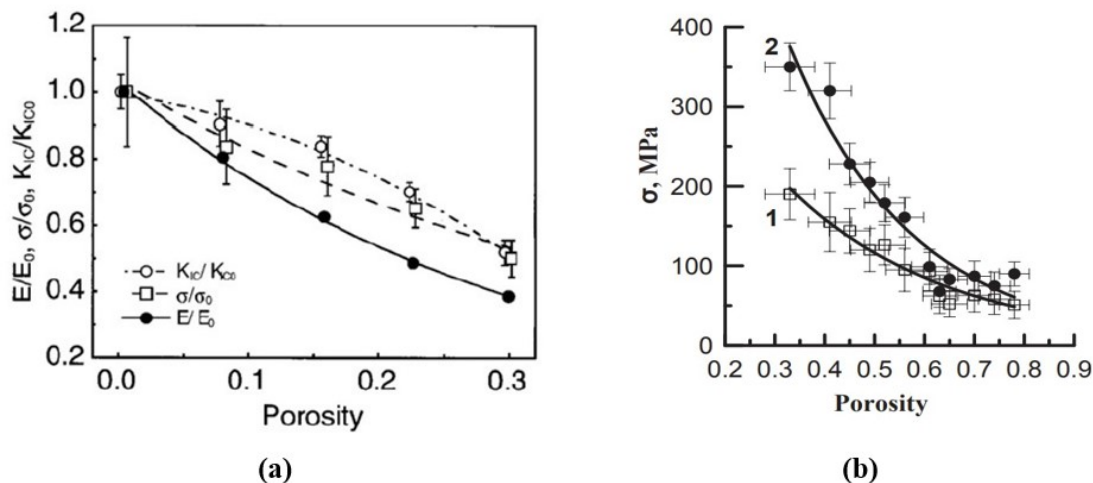


Figure 2.13 (a) Relative Young's modulus E/E_0 , flexural strength σ/σ_0 and fracture toughness K_{IC}/K_{IC0} as a function of porosity for silicon nitride-based ceramics [46]. (b) Effect of porosity on $\text{ZrO}_2(\text{Y}_2\text{O}_3)$ [47].

At lower levels of porosity, further heating to reduce porosity commonly leads to grain growth and the attendant sweeping of grain boundaries past previously intergranular pores. In many cases, the resultant intragranular pores are less detrimental to properties, and they may even be able to possibly counteract some reductions in properties that are caused by grain growth. In spite of the fact that this strategy of accepting some residual porosity, particularly intragranular porosity, ultimately results in the limitation of properties, it frequently emerges as a significant factor in the production of bulk ceramics [48].

Grain or particle related parameters still frequently affect properties in cases where porosity is required for functions, but these effects are typically secondary to those of the pore structure and typically occur at fine grain and particle sizes. Due to low processing temperatures used to control grain or particle growth, and in the common case of sintering, starting with fine particles, obtaining such fine sizes frequently necessitates maintaining significant porosity. However, grain size effects must also be taken into account, especially as porosity decreases, as it is extensively covered elsewhere. This is because some growth of grains, particles, or both occur, often inversely to the level of porosity [48].

2.5 Fundamental principles in capillary phenomena

Capillary phenomena arise when a liquid comes into contact with a porous material with open pores permitting fluid flow. The open pores could be assimilated as a group of small tubes where the capillary action is influenced by various factors, such as the surface tension of the liquid, the wetting properties of the solid surface, and the geometry of the capillary. The single capillary tube model of imbibition is a classic example used to explain the fundamental force interaction pertaining to capillary phenomena.

This model uses a capillary tube with a small diameter that is partially submerged in a liquid, while the other end of the tube is opened to air. The interaction between the cohesive and adhesive forces inside the tube causes the liquid to rise gradually against the gravity force as represented in Figure 2.14.

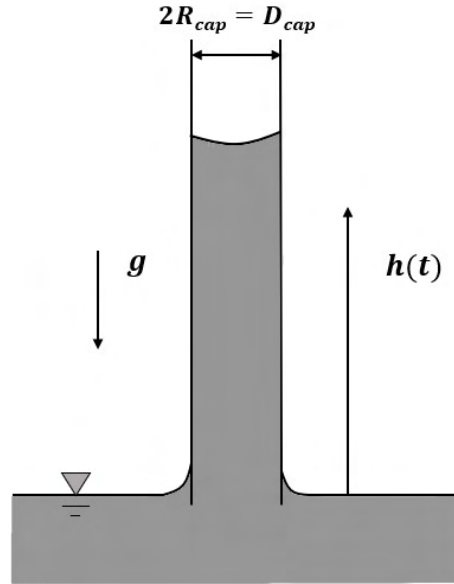


Figure 2.14 Liquid rise in a capillary tube with an inner radius R_{cap} . The gravity acceleration vector g points in the opposite direction of the fluid flow. The height of the liquid column varies with time and is represented by $h(t)$.

Cohesive forces refer to the attractive forces between molecules of the same substance, while adhesive forces refer to the attractive forces between molecules of different substances. In the case of the single capillary tube model, the cohesive forces within the liquid and the adhesive forces between the liquid and the surface of the tube cause the liquid to rise up the tube. The maximum height to which the liquid will rise in the tube is influenced by several morphological factors, including the diameter of the tube and the wetting properties of the fluid on the tube surface.

The smaller the diameter of the capillary tube, the higher the liquid will rise due to the increased capillary action. Similarly, the more the liquid wets the tube surface, the higher it will rise due to the increased adhesive forces. Capillary phenomena have many practical applications in various fields. In medicine, capillary action is used for blood glucose testing, where a small amount of blood is collected into a capillary tube and analyzed. Capillary action is also used in ink pens, where the ink is drawn into the nib through a capillary tube.

Capillary action plays a vital role in plant physiology, where it facilitates the transport of water and nutrients from the roots to the leaves. In industry, capillary action is utilized in oil recovery, papermaking, and the production of microfluidic devices, among others. In summary, capillary phenomena are fundamental to many aspects of our lives and an understanding of these phenomena is crucial for the development of new technologies and novel applications.

2.5.1 Surface tension

There is a mutual attraction between molecules in a fluid. This attraction is overcome when the molecules are subjected to enough heat (thermal energy) to cause them to transform into gaseous phase. While water molecules in the bulk of fluid are surrounded by attractive neighbors, those on the surface have less of them and are in an energetically unfavorable condition due to their isolation (Figure 2.15). As the fluid tends to adopt a configuration of low energy, the interface energy is minimized by reducing the area of the interface. A higher intermolecular interaction and a smaller molecular size lead to higher surface tension [49].

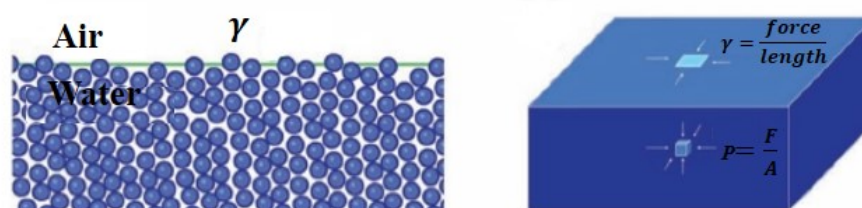


Figure 2.15 (a) Shows the free surface between air and water at the molecular scale. (b) Shows the characteristics of surface tension that is analogous to a negative surface pressure [49].

The interfacial tension between two fluids is a physical phenomenon that arises from the difference in energy per unit area, noted γ , that acts to oppose the formation of a new interface. We say that two fluids are miscible if there is no appreciable increase in the interfacial tension between them. Because γ is measured in terms of force per unit length or energy per unit area, surface tension could also be considered as surface pressure or, alternatively, as a line tension operating in all directions parallel to the surface.

2.5.2 Wettability and contact angle

When a liquid phase makes contact with a solid flat surface surrounded by a vapor phase, an equilibrium is established at the three-phase boundary between the liquid, vapor, and solid phases (Figure 2.16). The contour of the liquid phase adapted itself more easily for the minimization of surface energy because the cohesive forces between liquid molecules are weaker than those of the solid phase. Then the liquid phase tends to adopt a spherical shape.

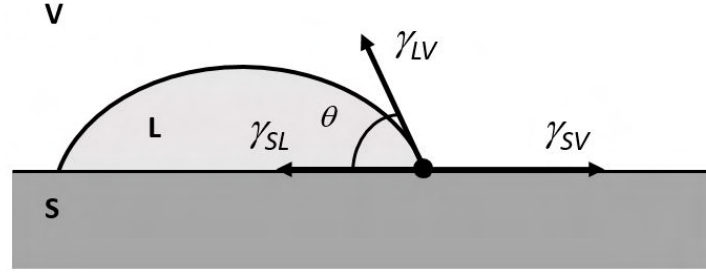


Figure 2.16 Contact between solid, liquid, and vapor phases. The equilibrium configuration between the three phases is produced under the horizontal components of the surface tension balance [50].

From the surface tension vectors characterizing the solid-liquid (SL), liquid-vapor (LV), and solid-vapor (SV) at the three-phase boundary, one can express the equilibrium balance of the horizontal components in the following Young's Equation 2.3. Subatomic disturbances in the solid at the site of fluid contact provide a downward force to counteract the vertical component from the liquid-vapor interfacial tension, allowing for a force balance in the vertical direction [51].

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad (2.3)$$

The contact angle θ of a liquid to a solid substrate is a measure of the wettability of a liquid on a solid. It corresponds to the angular separation between the liquid-vapor and solid-liquid interfaces. This angle is traditionally measured through the fluid phase since it is the denser of the two liquid and vapor phases. For example, for a water drop (L) in contact with a solid in air (V), it is through water that the contact angle is determined. When two non-miscible liquid phases (oil and water for example) are in contact with a solid substrate, the same rule is applied, the wetting angle is measured through the denser fluid (water in this case). The wettability is dependent on the contact angle that lower the contact angle results in better densification of the matrix [52, 53] .

A liquid phase having a low surface tension has a tendency to spread more easily on a solid substrate because it necessitates less energy in the production of a larger liquid-vapor surface. As a result, the wetting angle θ is small. The wetting angle is then a useful parameter to characterize the wetting of fluid on a solid substrate. As shown in Figure 2.17, when the contact angle θ is null, the liquid wets perfectly the surface. For a value of θ smaller than 90° , the liquid is wetting the solid substrate partially.

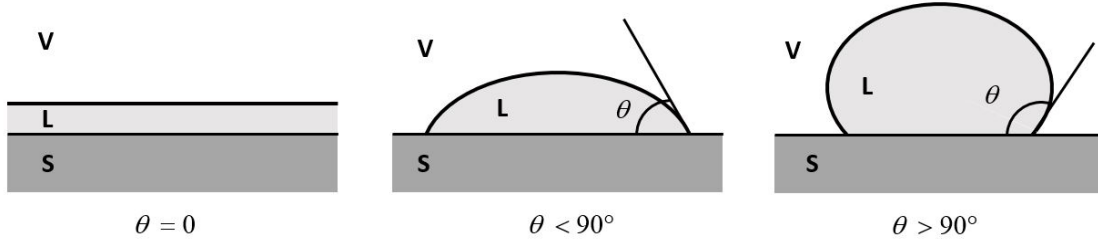


Figure 2.17 Contact angle θ for different wetting conditions. Left: perfectly wetting fluid; center: partially wetting; right: non-wetting condition.

The capillary phenomena that will be described in the present thesis correspond to that situation. The case of θ larger than 90° corresponds to the non-wetting condition. Some factors can modify the contact angle even if the nature of the liquid, vapor, and solid substances are kept the same. For example, the contact angle is known to diminish when the temperature increases. The surface finish of the solid surface influences also the wetting angle.

2.5.3 Contact angle and surface roughness

When a rough surface is wet, the effective contact angle shifts as the water molecules move from one contact point to the next. On a surface with a rough texture, the contact angle seems to be different than that on the same solid material with a flat surface. For characterizing a rough surface, one can define the following roughness parameters [49]:

$$\phi_r = \frac{\text{Total surface area}}{\text{Projected surface area}} > 1 \quad (2.4)$$

$$\phi_s = \frac{\text{Area of islands}}{\text{Projected surface area}} < 1 \quad (2.5)$$

The roughness parameter ϕ_r has an effect on the contact angle by including the surface energy throughout the entire rough surface area. On the other hand, the roughness parameter ϕ_s considers only the contact surface of islands associated with the pillars of surface relief.

For a wetting fluid ($\theta < 90^\circ$), the roughness parameter $\phi_r > 1$ does increase the hydrophilicity of the surfaces tending to reduce the apparent wetting angle. As shown in Figure 2.18, Wenzel's state corresponds to the full wetting of the rough surface. Depending on the scale of roughness, the apparent wetting angle θ_W could be smaller than that for a flat surface. Further to adhering to the surface's ridges and valleys as in Wenzel's relation, the liquid may suspend a composite surface consisting of the solid material and air pockets, corresponding to Cassie and Baxter's state.

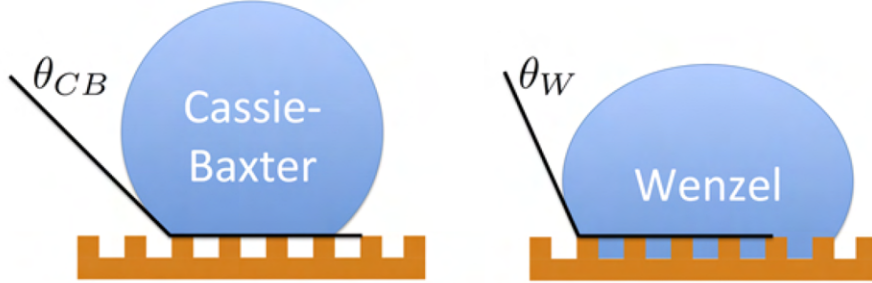


Figure 2.18 Wetting conditions corresponding to Cassie and Baxter's state and Wenzel's state [54].

In the Cassie and Baxter condition, the hydrophobicity of the surface increases ($\theta \rightarrow \theta_{CB}$) and a drop of liquid may slip off easily because of the limited solid-liquid contact surface.

Furthermore, the triple line or contact line describes the intersection of the three phases of development. The movement of the contact line when the fluid flows on the rough surface generates a dynamic contact angle that is different than the one at static equilibrium. In conclusion, the contact angle is a critical factor to consider when characterizing surfaces and understanding the wetting behavior of liquids on rough substrates that are characteristics of granular porous media.

2.6 Capillary imbibition

Capillary imbibition is described as the process by which a fluid flows in a solid tube as a result of surface tension forces that could be partially counteracted by other forces or phenomena (viscous, inertia, or gravity forces).

2.6.1 Capillary pressure

When a wetting liquid phase enters the extremity of a capillary tube, capillary forces are generated due to differences in surface energies of the solid and liquid phases (Figure 2.19). The meniscus that is formed at the surface of the liquid, characterized by the wetting angle θ ,

leads to a vertical surface tension γ_{LV} component along the periphery of the inner surface of the tube that pulls the liquid upward. This resulting force can be associated with a capillary pressure P_c at the liquid-solid interface described by the following Young-Laplace Equation [55].

$$P_c = \frac{2\gamma \cos \theta}{R_{cap}} \quad (2.6)$$

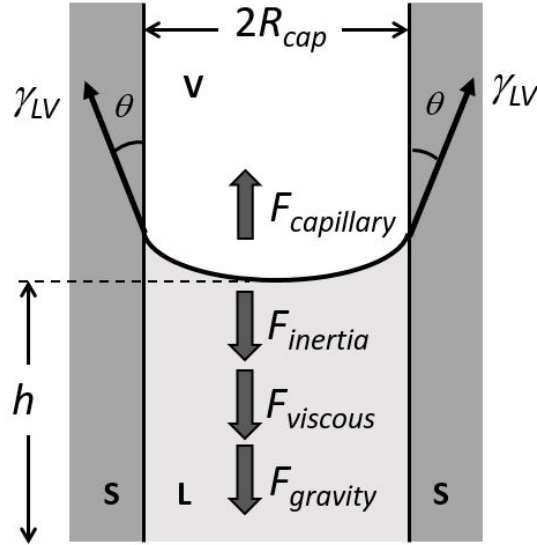


Figure 2.19 Liquid meniscus generated by the liquid-vapor interface of a wetting liquid in a single capillary tube. Representation of the balance of forces acting on the liquid-vapor interface leading to capillary imbibition.

One of the most difficult aspects of applying the Young-Laplace equation for capillary pressure (Equation 2.6) is estimating the capillary radius R_{cap} . Because real porous media with convoluted, linked fluid channels are not like bundles of identical, aligned capillary tubes, some assumptions must be made to determine the comparable capillary radius.

By counteracting the upward force caused by capillary pressure with the downward force caused by gravity, the capillary rise experiment provides the most precise estimate of the equivalent capillary radius as already exhibited in published researches [56,57]. This capillary radius has been denoted by dry radius [58], or static radius [59].

2.6.2 Equation for capillary imbibition dynamics

The simplest capillary imbibition model was described by Lucas and Washburn which corresponded to the simplified single capillary tube configuration. The primary driving force, in this case, is the capillary pressure with effective resistance to imbibition posed by the viscosity of the fluid [60].

However, in a more general approach, it is necessary to consider the three major contributors to the capillary flow: inertia, viscous, and gravity forces (Figure 2.19).

$$\sum \vec{F}_{ext} = \vec{F}_{viscous} \cdot V + p_c \cdot \vec{S} + m \vec{g} = \frac{\partial(m, \vec{v})}{\partial t} \quad (2.7)$$

The development of capillary flow and its transition from one stage to another becomes important for quantifying and comprehending the dynamics of complex phenomena. The most fundamental concept in the capillary flow is the balance of momentum inside a capillary tube by the various types of forces given by the equation:

$$\frac{2\gamma \cos \theta}{R_{cap}} = \frac{d(\rho h \dot{h})}{dt} + \frac{8\eta h}{R_{cap}^2} \dot{h} + \rho g h \quad (2.8)$$

Here the term $\frac{2\gamma \cos \theta}{R_{cap}}$ denotes capillary pressure, $\frac{d(\rho h \dot{h})}{dt}$ is related to the inertial force, $\frac{8\eta h}{R_{cap}^2} \dot{h}$ is related to the viscous force and the last component $\rho g h$ is related to the gravitational force [61]. The height of the liquid column is given by h and the velocity of the capillary rise is given by $\dot{h}$. Equation (2.8) can be solved in order to find a relation of the type $h = f(t)$ for determining the kinetics of capillary rise by evaluating the following expression:

$$\rho \frac{\partial(h.v)}{\partial t} = -\frac{8\mu}{r^2} h.v + \frac{2\gamma \cos \theta}{r} - \rho g h \quad (2.9)$$

By neglecting the gravity effects, the following Washburn's equation is obtained :

$$\frac{h^2}{t} = \frac{\gamma \cos \theta}{4\eta} d_{eff} \quad (2.10)$$

In the following paragraphs, Equation (2.8) will be solved based on assumptions such as there are no inertial or entry effects in the liquid reservoir and the viscous pressure loss inside the capillary tube is given by the Hagen-Poiseuille law (representing the second term in Equation (2.8)). It is also assumed that the fluid is incompressible, the flow is laminar, capillary pressure is constant for stationary meniscus and it is calculated in this case using the static contact angle θ and the radius R_{cap} .

Although these assumptions are too generic and have little significance to the actual granular capillary phenomena due to oversimplification of the poral network, they are necessary to understand the basic interplay of forces acting that generates the capillary action in a porous media.

2.6.3 Capillary imbibition regimes

The various inertial regimes for capillary-induced flow are presented in Figure 2.20 to understand the outcome of the interplay of various forces in wicking dynamics. These regimes are also described based on different instances of time in the evolution of the capillary flow. These regimes have been separated based on the transition from one dominant force to another. The change is seen as smooth, but the fluid meniscus jumps up at first. This meniscus then develops into a diffuse-type forward front and a macroscopic front, which correspond to a higher degree of saturation. A short description of the four main regimes is given below.

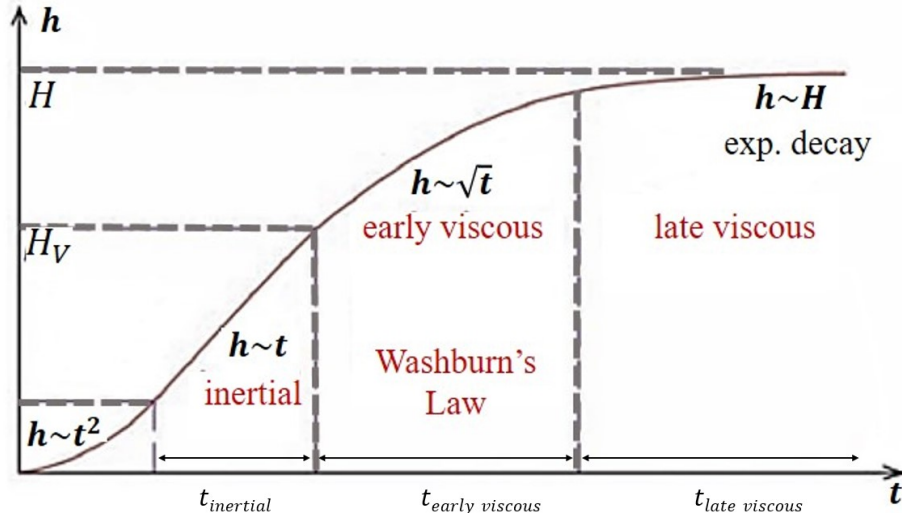


Figure 2.20 The different regimes for capillary rise dynamics show the evolution of wicking from inertial to viscous to exponential decay in the rate of imbibition [62]. For illustration purpose, note that the vertical scale for the capillary height and the horizontal scale for time is not linear.

1. **Early inertial regime:** The inertial flow regime arises after the sudden imbibition of fluid at the initial stage where the inertial time scale ($\Delta t_{inertial}$) is much shorter than the viscous time scale ($\Delta t_{viscous}$); the imbibition is then dominated by inertial forces. In this regime, the viscous and gravity forces could be neglected. Resolving the flow Equation (2.8) leads to a relation between h and t of the type $h \propto t^2$.
2. **Inertial regime:** The complex phenomena occurring during this regime are due to the beginning of the effect of viscous forces while the Poiseuille flow is developing at the

entry of the capillary tube. This progresses to a fully developed region. At the end of this regime, the viscous force becomes dominant and the inertial force can be neglected. For this late part of the inertial regime, the capillary height h increases proportionally with time t :

$$h = \sqrt{\frac{4\gamma \cos \theta}{\rho R_{cap}}} t \quad (2.11)$$

Practically, by taking into account typical values for the properties of small capillary tubes and for the wetting fluids that will be targeted in the present study, the time scale for the two first regimes is extremely small. The impact of these two first regimes could then be neglected.

3. **Early viscous regime:** This regime corresponds to the flow where the capillary pressure is opposed only by the viscous effect. From Equation (2.8), by neglecting the inertial and gravitational forces and posing the equilibrium between the capillary pressure and the Hagen-Poiseuille viscous effect, we obtain:

$$\frac{2\gamma \cos \theta}{R_{cap}} = \frac{8\eta h \dot{h}}{R_{cap}^2} \quad (2.12)$$

where η is the viscosity of the fluid (Pa.s). By integrating Equation 2.12, we obtain the Lucas-Washburn law where the evolution of h as a function of time is given by:

$$h = \sqrt{\frac{\gamma R_{cap} \cos \theta}{2\eta} t} \quad (2.13)$$

That condition is characterized by a fully developed region of flow. The capillary imbibition is described by a diffusive type law where the impregnated height is directly proportional to the square root of the impregnation time [63].

$$h \propto \sqrt{t} \quad (2.14)$$

This regime will characterize most of the practical test conditions that will be observed in the present research work.

4. **Late viscous regime:** As the height of the capillary column increases, its weight becomes less negligible and it is necessary to consider the gravitational force. In the late viscous-gravitational regime, the relation between the column height h and the

time t corresponds to exponential decay. The fluid rise stops when the gravitational force is large enough to balance the capillary pressure. This leads to the evaluation of Jurin's height H_J :

$$H_J = \frac{2\gamma \cos \theta}{\rho g R_{cap}} \quad (2.15)$$

For example, by considering the properties of hexadecane as wetting fluid and a diameter of 200 nm for capillary channels in SiC granular materials, Jurin's height is in the order of 80 m. So it is considered that for capillary rise height $h < 0.1H_J$, the gravitational effect could be neglected, which corresponds to the experimental conditions that will be carried out in the present research work.

2.6.4 Capillary imbibition in uniform circular capillaries

The culmination of several forces acting in tandem with each other at different time instances and scales within the porous structure causes capillary rise. This is strongly dependent on the macro, microporous network, and their spatial distribution, the morphology of the pores (open, closed), the nature of the fluid, and time [64].

Most of the traditionally defined models (eg. the capillary tube model) are able to explain the capillary rise dynamics in an overly simplified manner. Several investigations have shown that the imbibition process in cylindrical tubes may be broken down into the four distinct regimes presented above, which they have labeled as follows: the inertial regime, the viscous and inertial regime, the purely viscous regime, and the viscous and gravitational regime [65–67].

The different single uniform circular capillary rise models concentrate on different time stages of the complete imbibition regime. The different time stages are used in conjunction with the incorporation of different force components from gravity, inertial and viscous regimes. The different approaches with the corresponding time stages is given in Table 2.3:

Capillary model	Viscous	Gravity	Inertia	Application time stage
Quere [65]			✓	$0 < t \leq \frac{0.0232R_{cap}^2\rho}{\eta}$
Bosanquet [66]	✓		✓	$\frac{0.0232R_{cap}^2\rho}{\eta} \leq t \leq \frac{R_{cap}^2\rho}{16\eta}$
Lucas-Washburn [68, 69]	✓			$\frac{R_{cap}^2\rho}{16\eta} \leq t \leq \frac{2.1151R_{cap}^2\rho}{\eta}$
Fries and Dreyer [61]	✓	✓		$\frac{2.1151R_{cap}^2\rho}{\eta} \leq t \leq t_{eq}$

Table 2.3 The capillary imbibition models' applicability range in terms of time scale. t_{eq} represents the time it takes for the liquid column to reach Jurin's height. [70].

A number of other significant works have been completed that provide us with a clearer approach to the inclusion of the imbibition regime corresponding to the time stage, also the combination of different force components for capillary imbibition has been analyzed and solved. The contributions of those research are given in Table 2.4 which demonstrates the different scopes of applications for the different uniform circular capillary rise models.

Capillary model	Application scope with remarks
Quere et al. [67]	Parabolic trajectory of oscillations in low viscous fluid
Szekely et al. [71]	Improvements in the inertial term
Zhmud et al. [72]	Refinement of viscous term, less coherence with physical definition
Levine et al. [73]	Motion of fluid at the entry and exit of capillary tube

Table 2.4 Supplementary works on capillary rise models in the circular capillary giving different application scopes [70].

2.6.5 Imbibition dynamics in bi-disperse capillary tubes

To model a porous material containing different sizes of pore channels, it becomes necessary to consider capillary tubes with different diameters. This approach was taken by J. Bico and D. Quéré [63] where they model the relative progression of the liquid front in a bi-disperse capillary model (gravity was neglected). As shown in Figure 2.21, the model of bi-disperse tubes is seen as two interconnected tubes of different radii ($r_{cap} < R_{cap}$) permitting fluid flow at the interface between them. These tubes were brought in contact with a wetting liquid. As the liquid infiltrates the tubes, it is supposed that the height at the time t is not the same for the adjacent tubes, due to the difference in the capillary pressures generated in the two tubes.

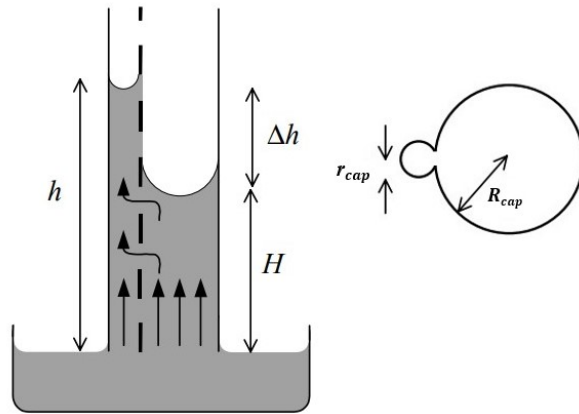


Figure 2.21 Bi-disperse model with the representation of the two scales of the tube radius [63].

If the tubes were not interconnected and acted independently on the rising fluid, the smaller tube would exhibit a slower rise of the infiltrating fluid due to higher friction, since the diffusion coefficient in Washburn's law (Equation 2.13) scales as the square root of the radius of the tube. Because the tubes are interconnected, the pumping of the liquid from the tube having the large radius reduces the viscous dissipation in the smaller tube [63].

On the side of the larger capillary tube, the viscous loss can be expressed according to Poiseuille law as:

$$\Delta P_1 = \frac{8\eta H}{R_{cap}^2} \frac{dH}{dt} \quad (2.16)$$

The liquid in the large tube is mainly driven by the Laplace pressure ($2\gamma/R_{cap}$), which leads to Washburn's equation:

$$H = \left(\frac{R_{cap}\gamma}{2\eta} \right)^{1/2} t^{1/2} \quad (2.17)$$

The smaller capillary tube with radius r_{cap} is filled from lateral flow from the larger tube up to height H observed in the tube of radius R_{cap} . The additional height Δh for the progression of liquid occurs with a mean velocity given by dh/dt due to the Poiseuille viscous dissipation expressed by:

$$\Delta P_2 = \frac{8\eta\Delta h}{r_{cap}^2} \frac{dh}{dt} \quad (2.18)$$

The Laplace pressure pulling the fluid in the smaller tube corresponds to the difference between the pressures in both tubes resulting in:

$$\Delta P_2 = 2\gamma \left(\frac{1}{r_{cap}} - \frac{1}{R_{cap}} \right) \quad (2.19)$$

Resolving for the evolution of $\Delta h = h - H$ as a function of time from the preceding Equations, we obtain:

$$\Delta h \approx \left(\frac{\gamma r_{cap}^2}{2\eta R_{cap}} \right)^{1/2} t^{1/2} \quad (2.20)$$

Thus Δh is found to be positive where the liquid in the smaller capillary tube progresses faster and is also diffusive in time. It appears that the relative value of the extra height Δh

in smaller capillary tube scales with the ratio of radii on both sides:

$$\frac{\Delta h}{h} \approx \frac{r_{cap}}{R_{cap}} \quad (2.21)$$

In a porous specimen having an interconnected network of macro and micropores, the capillary flow would behave in a somewhat similar manner as described in the bi-disperse medium. This could eventually result in porous zones filling at different speeds.

2.6.6 Capillary imbibition in uniform non-circular capillaries

The modeling of granular porous materials by using straight capillary tubes with circular sections is an oversimplification of the reality where the pore channels are delimited by small bonded particles. The sections of the channels are then far from circular and they vary along the channels, which makes them non-uniform. A lot of significant research work has been performed in the classification of capillaries based on geometric shapes. The uniform capillaries with non-circular sections comprise primarily triangular, rectangular, and square capillaries [74–77].

For the overall description of the capillary flow in non-circular tubes, the modeling of Hagen-Poiseuille law and capillary pressure [70] is done by introducing a shape factor for differentiating the behavior of non-circular section from that of circular section. This results in a slightly lower capillary pressure for non-circular sections having internal corners. In the event that the contact angle θ between the liquid and the solid phase is less than 90° , the wetting phase enters the circular capillary in an unprompted manner. In capillary tubes having internal corners, the liquid tends to moisten the inside corners of the capillary first and lead to the liquid front advancing as reported by Concus and Finn [71]. The researchers Ouali et al. [77] conducted an experiment in which they observed that the wetness at the corners of square capillary tubes causes the liquid fingers to extend beyond the main meniscus (Figure 2.22).

Both the corner flow and the bulk flow may be broken down into their respective components inside a capillary channel that has an internal corner. In the absence of gravity, horizontal capillary tubes exhibit a connection between corner and bulk flow where the latter follows the Lucas-Washburn (LW) $t^{1/2}$ scaling rule. Dong and Chatzis [78] observed that the expansion of the corner flow in the horizontal square channel likewise follows the $t^{1/2}$ scaling rule after they included the dimensionless flow resistance into the imbibition of pure corner flow.

Rye et al. [79] discovered that the time dependency of infiltration length in the capillary imbibition process follows the $t^{1/2}$ scaling law. Open triangular capillaries, which are also known as horizontal V-shaped grooves, are the focus of this study. The capillary pressure

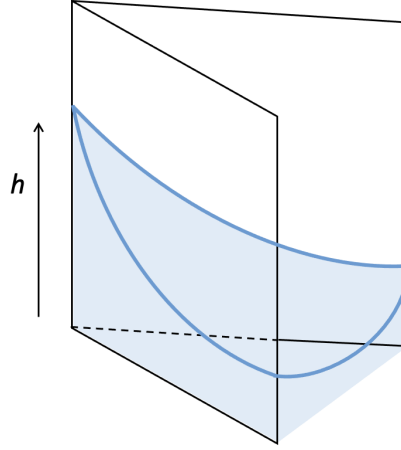


Figure 2.22 Visual representation of capillary flow in a corner of a non-circular tube section. The liquid phase appears in light blue.

at the corner of the V-shaped groove causes the overall flow to move forward, and this flow may be thought of as the coupling flow that connects the corner and the bulk flow.

Tas et al. [80] investigated the imbibition of demineralized water into air using nano-fabricated rectangular capillaries. Their findings suggest that the measured imbibition rate is lower than the rate predicted by the LW model. Han et al. [81] conducted extensive experiments on the filling kinetics for capillaries of varying sizes and configurations. The location of the fluid flow could be used to verify the $t^{1/2}$ scaling rule, which is consistent with the LW kinetics law. According to the findings of the aforementioned experiments, the flow in the horizontal square and rectangular capillaries adhered to the $t^{1/2}$ scaling rule, regardless of whether or not corner flow was taken into account.

Other capillary imbibition models were developed for square and rectangular capillaries. The imbibition model of a circular capillary to a rectangular microchannel was created by Ichikawa et al. [82]. In both the circular tube and the rectangular micro-channel, it has been found that the connection between non-dimensional time and interface location is the same. A theoretical model for flow in rectangular capillaries under the impact of capillary and gravity forces was presented by Jong et al. [83]. As described previously, when the gravitational forces can be neglected, the capillary imbibition kinetic follows the $t^{1/2}$ diffusive scaling law. Under the effect of gravity, Ponomarenko et al. [84] showed that the capillary imbibition along a vertical internal corner follows the $t^{1/3}$ scaling law.

2.6.7 Capillary imbibition in non-uniform section tubes

Capillary channels found in granular porous materials can exhibit variations in their cross-sectional geometry along their length, which can add a level of complexity to their description. In this case, the effective flow is influenced by the varying cross-section, which changes the capillary radius and pressure as the fluid progresses through these geometries. In non-uniform capillaries, the inclusion of tortuosity (see definition in Section 2.7.1) becomes significant as it becomes an important parameter to quantify the capillary flow based on the real poral network that is generated by interconnected open pores. All these changes in the geometry could be reduced to the definition of an effective hydraulic radius for the poral network.

Using the Hagen-Poiseuille equation and factoring in the effects of gravity, Czachor [85] derived the capillary rise law for the sinusoidal convergent-divergent capillary (Figure 2.23). The analytical equation relating capillary pressure and volume velocity of a Newtonian fluid in five capillaries with varied converging-diverging axisymmetric geometries was derived by Sochi [86]. Then, a model was built to describe the connection between fluid qualities like Newtonian and non-Newtonian, and variables like pressure drop, volume velocity, and the velocity in convergent and divergent capillaries [87]. In all cases, if an effective hydraulic radius is considered and if the gravity is neglected, the capillary imbibition along the pore channel follows the $t^{1/2}$ scaling law.

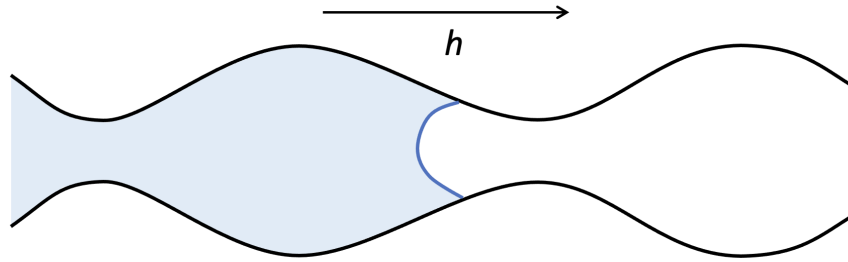


Figure 2.23 Capillary flow in a sinusoidal convergent-divergent capillary tube for a wetting fluid (light blue).

2.7 Capillary flow in porous media

In most practical domains where capillary flow occurs, the representation of porous materials as a bundle of parallel fine capillary tubes is too simplistic. As described in Section 2.4, the different sizes and shapes of open pores in the microstructure of porous materials such as ceramic matrix composites lead to the definition of various levels of capillary pressures resulting in the porosity zones that could be partially saturated by fluid imbibition.

The wetting of a porous medium by a fluid phase is closely related to capillary actions in which the medium is originally dry. The parameters controlling the capillary phenomenon can be observed at different scales: from the molecular scale, which governs chemical and molecular interactions very close to the solid-liquid-air interface, to the pore scale, where surface energy considerations result in contact angles and menisci, all the way up to the representative volume element (RVE) scale, where macroscopic saturation is observed [88].

There are still many unanswered questions regarding the relationship between the geometric and thermodynamic factors operating at these length scales. Capillary forces play a significant part in several physical systems where a fluid invades a network of small gaps, guaranteeing fluid circulation in plants, in the lachrymal ducts, wicks, brushes and towels, heat pipes, fountain pens, and, of course, at the basis of hydrogeology and groundwater movement [89, 90].

2.7.1 Tortuosity

The tortuosity is an important parameter affecting the fluid flow conductivity in a porous material. Even if the definition of tortuosity is not consistent from one reference to the other, it could simply be defined on a geometrical basis as the ratio of the average flow path length to the straight path length across the porous medium [91]. This definition neglects the variations in the cross-section of the flow along the porous channels. The adimensional tortuosity number τ is therefore larger than 1 in typical open pore networks. Even if this definition is simplistic in principle, it is very difficult to apply in practice since the pore network of real porous materials is very complex to model precisely.

Another factor that makes the definition of tortuosity more complicated is its strong dependency to the saturation level and to the type of transport relationship involved in the physical description of the phenomenon [91]. For example, whether the context applies to transport of fluid, electrical charges, chemical species or heat, this could lead to the definition of hydraulic, electrical, diffusional and thermal tortuosities, respectively [92]. Contrary to the definition of geometrical tortuosity that depends only on the porous microstructure, the flux-based definitions related to physical phenomena depend on the porous microstructure and the transport flow characteristics (permeability, diffusivity and conductivity). From the modelling of different physical phenomena, the definitions of tortuosity give invariably a value in the order of 2 for porous materials with an open porosity in the order of 40–50 % [91]. For that reason, the methods of evaluation are interchangeable in literature when values for tortuosity should be determined [92]. The tortuosity values are then considered as tuning parameters (often defined as *fudge factors*) to take into account the complex flow paths in porous materials.

The development of explicit models to evaluate the tortuosity in the context of capillary flow in porous media is extremely challenging since it depends on empirical coefficients that are difficult to characterize for complex pore structures. Nevertheless, some efforts were deployed to at least identify the main parameters that condition the evaluation of tortuosity. By considering the Kozeny-Carman approach related to the permeability K of a porous material [93], one can find the following relationship between the tortuosity τ and the pore network characteristics:

$$\tau \propto \frac{\varepsilon d_{50}^2}{K} \quad (2.22)$$

where ε is the porosity, d_{50} is the diameter of capillary channels and K (m^2) is the permeability. In the case of bundles of identical straight capillary tubes, Equation 2.22 for $\tau = 1$ led to the simplified relation developed by Dullien [43]. Different models also gives a variety of porosity functions instead of the simple parameter ε as shown in Equation 2.22. However, it is quite intuitive to understand that tortuosity scales with the inverse of permeability. This is also true when the tortuosity model is based on compact poly-dispersed granular materials.

2.7.2 Capillary flow in unsaturated media: Richards equation

The Lucas-Washburn (LW) equation which is used to model fluid transmission through porous media takes into consideration three assumptions: uni-directional flow, separate zones of complete and dry porous media, and pore geometry idealized as a collection of capillary tubes in parallel that have an equal radius. The LW equation is adapted for uni-directional imbibition, leading to the formation of a sharp flow front between wetting (liquid) and non-wetting (gas) fluids. As shown in Section 2.6.3, this simplistic approach to explain the capillary flow led to the diffusive law ($h \propto \sqrt{t}$) to describe the kinetic of capillary rise.

To model more precisely a porous material without specifying the geometrical arrangement of pore channels, one could use the Darcy's approach where the open porosity is characterized in terms of its permeability. The following extended Darcy's law describes more precisely the unsaturated flow of a fluid in porous media [94]:

$$q = -k(s)\nabla h \quad (2.23)$$

Where q is the volume of fluid passing through the unit area in unit time (m/s), $k(s)$ is the hydraulic conductivity (m/s) of unsaturated porous granular media as a function of s , the volume fraction saturation or moisture content and h the total liquid head (m). When this is inserted in the continuity equation for mass conservation, we obtain the so-called Richards

equation [95]]:

$$\frac{\partial s}{\partial t} = \nabla(D(s)\nabla s) \quad (2.24)$$

where $D(s)$ represents the capillary diffusivity that depends on the fluid properties (viscosity, surface tension, density), the poral network characteristics of solid media (porosity, median pore size, tortuosity) and the saturation level s :

$$D = \frac{K}{\varepsilon\eta} \frac{\partial p}{\partial s} \quad (2.25)$$

Here, K is the permeability (m^2) of the porous media, ε the porosity and η the viscosity ($\text{Pa}\cdot\text{s}$) of the fluid. To completely solve the non-linear partial differential Richards equation, it is necessary to model the closure relationship between the local fluid pore pressure p and the saturation level s . One of the closure relationship that could be used is the following Van Genuchten function [96]:

$$p\alpha = \left(s^{-1/m} - 1\right)^{1/n} \quad (2.26)$$

where $m = 1 - 1/n$, n and α are empirical parameters. It is interesting to note that solving the Richards equation for porous media subjected to capillary imbibition leads also to a diffusive law of the type $h \propto \sqrt{t}$ for the capillary rise kinetic. So, contrary to the necessary hypotheses for obtaining the LW equation, it is not necessary for Richards equation to formulate any hypothesis on the pores size or shape. The only thing to consider is the unsaturated flow at the interface between liquid and gas (variable s) that becomes diffuse instead of abrupt ($s = 0$ or 1). In this approach, it is important to consider that the transport properties of the fluid, such as the capillary diffusivity, depends on the degree of saturation.

Ashari [97] solved the two-dimensional Richards equation for the thin fibrous sheet with random in-plane fiber orientation. The total volume of liquid absorbed into the sheet with respect to time was used to calculate the equivalent radius the liquid would occupy if a clear wet-dry boundary did exist in the domain. They then compared this equivalent radius, normalized with the radius of the fully saturated liquid source. He also observed that sheets favoring one in-plane orientation of fibers over another absorb more liquid over time.

Richards equation in one dimension was also solved by Jaganathan [98] for inclined fibrous sheets. He was able to predict the partial saturation zone. The different terms in the Richards equation are functions of saturation. This approach gives a very significant technique that

provides the ability to model saturation in a multidimensional media along with the influence of individual microstructural parameters.

2.7.3 Modeling and simulation of multiphase flow in porous media

Capillary effects play a significant role in polymer liquid resin processing, despite the fact that the magnitude of capillary pressure is relatively low when compared to the pressures that are applied, and while they primarily act on the yarn scale, they have a large influence on the quality of the final part on a macroscopic scale. So, capillary effects need to be taken into account in order to make reliable numerical models that can be used to explain and predict flow behavior in liquid composite molding [99].

Viscous, and capillary forces at micro- and mesoscale interact (compete for domination) to create voids whose size, position, and shape vary with the strength of the two types of flow. Researchers have looked into the causes, effects, and ways to get rid of voids in advanced composites, which are known to lower the mechanical performance of these materials by a large amount [100–103].

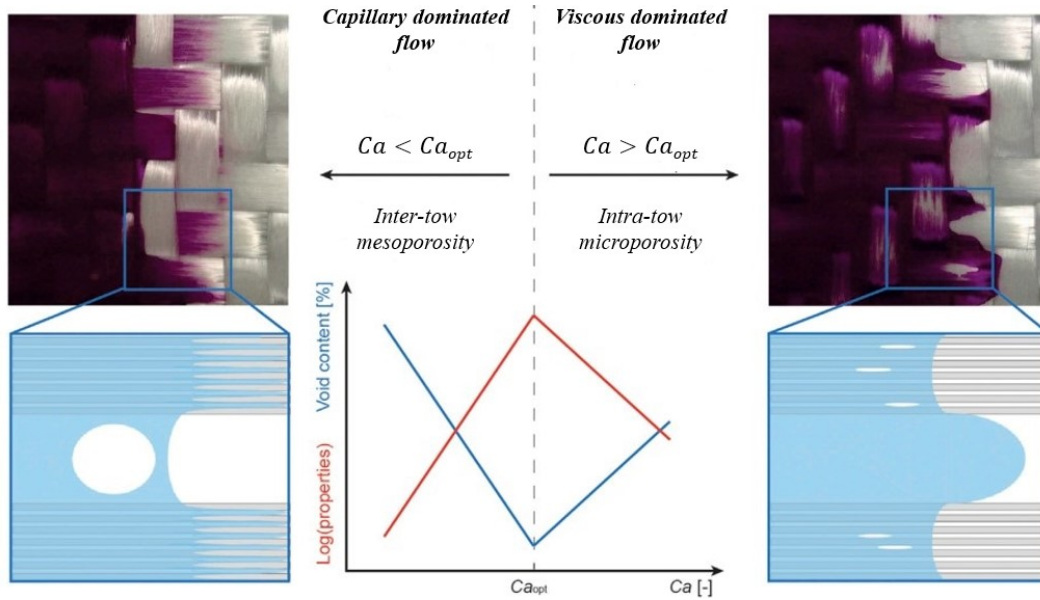


Figure 2.24 Capillary imbibition based on different void scales based on the comparison of optimum capillary number Ca_{opt} , the flow front profile varies with the capillary number within the multiphase void media [88].

Throughout the course of the last several decades, numerous strategies have been developed in the direction of the development of flow simulations. These strategies describe dual-scale flow behavior and the role that capillary effects play at various scales. Most ways of determining and comprehending the capillary effects are based on direct or indirect experimental

observations of that flow front location and saturation overtime during an infiltration experiment when no external body forces are acting on the system (other than gravity) [104].

Anisotropic pore networks are generally generated in and along the fibrous interface by vast inter-tow areas and tiny intra-tow regions (Figure 2.24), this is similar to the situation of rocks that often possess randomly dispersed micro and macro channels rather than well-organized poral structures [88]. Most of the time, fiber reinforcements used in high-performance composites have a bimodal pore distribution. Experiments have been done to characterize the relationship between void content and the capillary number Ca [105] defined as the ratio of viscous to surface tension effects. Experiments using capillary imbibition have been used to define the capillary pressure, which enables the pressure to be directly quantified based on a single experiment.

The spaces between individual fibers in tow are called micro-pores (intra-tow), while the larger spaces between tows are called meso-pores (inter-tow). This results in a dual scale flow during capillary imbibition as a result of this pore characteristic, which occurs regardless of the production technique [106]. Even though this imbibition might not be under full capillary forces, this multiphase infiltration would still go through all the different capillary imbibition regimes, as shown in Figure 2.20.

The process of impregnation is mostly driven by hydrodynamic forces that are caused by the difference in pressure. On the other hand, there is a noticeable increase in viscous drag in micro-pores, which are places where there is less permeability. Furthermore, capillary forces are present at the fluid/fiber interface. The connection between the permeability of the yarn, the total permeability of the preform, and the capillary effects result in a complicated relationship in terms of the relative influence of flow inside and between tows [88].

Amico and Lekakou proposed a methodology in which the axial impregnation of a fiber bundle [107] is simulated, for vertical axial capillary imbibition of a single fiber bundle with silicone oil. The graphical representation of the effect of permeability and capillary pressure simulations has been shown in Figure 2.25. It was observed that the order of magnitude of capillary pressure dictates the imbibition rate that has been dimensionally demonstrated while establishing the research context. They also conclude that for silicone oil or similar fluids, the Carman-Kozeny equation is recommended for the prediction of permeability κ .

Cagler and his team did experiments on the capillary rise with better wetting to learn more about dual-scale flow in a capillary-dominated regime. The optimal capillary number has also been discussed, corresponding to the lowest percentage of voids in composites. They also discussed the flow front morphology with the fiber phase. The surface texture of the fiber reduces the effective irregular surface, which also reduces the effect of rough edges on

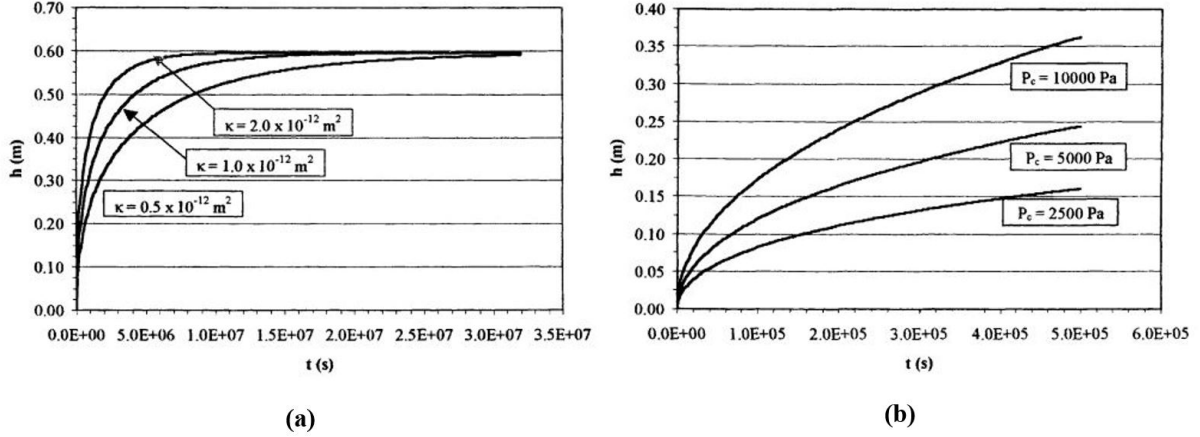


Figure 2.25 (a) Predicted curves for different permeability (κ) with constant capillary pressure (P_c) in axial capillary imbibition of a single fiber by silicone oil. (b) The imbibition rate increases with the rise in capillary pressure [107].

the preferential imbibition process. In the regime dominated by capillary forces, surface treatment enhanced the flow between and within the longitudinal and transverse bundles, resulting in faster impregnation [108].

Porosity found in composites is primarily caused by the impregnation of reinforcing fibers with fluid at two scales: inter-tow and intra-tow [109]. During the penetration of fluid at these sizes, viscous and capillary effects, which are connected by the dimensionless capillary number Ca [110, 111], compete with one another. Micro-porosity (intra-tow) can form when flow rates are high due to high permeability, but macro-porosity (inter-tows) form when the capillary flow is dominant and permeability is low. During impregnation, capillary effects must be taken into account, and their impact on the process must be determined using capillary pressure P_c . Local wetting impacts liquid/air surface tension, and differences in solid/liquid and solid/air surface energy generate this capillary pressure.

The capillary pressure is greatest when the permeability is lowest. This conclusion is consistent with the notion that capillary effects dominate viscous effects at extremely low permeabilities [112]. Since infiltration requires movement, the dynamic contact angle is a better way to describe how fluids and fibers can stick together. Still, it is hard to figure out analytically, so the static contact angle is usually just measured as a first guess. This is done even though the results may be very different from the values found by the dynamic analysis. To get over this obstacle, empirical rules like Tanner's law [113] have been offered in the body of academic work as a method for estimating the dynamic contact angle from the static one.

The Lucas-Washburn approach assumes that the shape of the porous medium stays the same

over the course of the experiment. It also doesn't take into account the forces of attraction between vertical surfaces caused by elasto-capillary effects, nor does it take into account the swelling effect in natural fibers that causes the densification effect. As a result, some modifications have been suggested over the years [114,115], that are necessary for precise representation of the poral network and will provide better control over the imbibition.

Modeling of unsaturated flow including capillary effects

Capillary forces are at work over a wide range of porosity scales (presented in Table 2.2) with poral morphology because partially saturated areas display a large distribution of pore channel widths. As a result, the capillary pressure that is represented in macroscopic studies is the average of several capillary pressure jumps that occur within a small region. Also, the gradual saturation is directly linked to a progressive filling of the pores, which can in turn be associated with void processes that occur during the infiltration [99,109].

The two-phase flow technique and the dual-scale approach are the two primary methods that are typically utilized to simulate the capillary imbibition phenomena in an unsaturated porous medium [116]. In certain circumstances, the flow of resin is modeled as a two-phase flow. The resin first penetrates the porous medium (the fiber phase), which then forces out and expels the fluid that saturates the porous medium (the gaseous phase). As previously mentioned, the fiber/matrix system as well as the impregnation circumstances (fluid velocity, dynamic contact angle) determine whether the substrate is wet or non-wet.

For simplicity, the resin is typically considered in the non-wetting phase. This is frequently seen to be the case in industrial liquid composite molding (LCM) processing when flow rates are high enough that the dynamic contact angle exceeds 90° . In the current approach that is being employed, permeability and pressure are determined by the degree to which the infiltrating fluid is saturated (s), and the total saturations of all phases add up to 1. Suppose the porous media is modeled as a random assembly of tubes with varied diameters. In that case, each of these tubes will imbibe the fluid in a unique way, which will result in a robust connection between the saturation and the capillary pressure.

The modeling can have two approaches that represent two different perspectives. Using mass balance equations and a single-phase Darcy's law, the two-pressure formulation describes the velocities of the two fluids passing through the same porous material while under different pressures. Assuming a low air pressure, the mass balance equation of resin simplifies to Richard's equation, which may be calculated without reference to any other variables [117]. The fractional flow technique is another option; in this case, saturation and pressure are treated as separate factors.

The Buckley-Leverett's formulation (which assumes an isotropic media) is used to determine saturation, while the gravitational and capillary forces are disregarded [118]. Recently, a numerical model based on this technique was provided by Gascón et al. [119] who accounted for capillary effects and the influence of residual air saturation. The saturated permeability, k_{sat} , and the relative permeability, k_r , a dimensionless number between 0 and 1 that is a function of s , are used to describe the permeability K in two-phase flow modeling. The relative permeability, denoted by the symbols k_r , characterizes the relative movement of fluid and air phases inside the porous media [119,120].

These models assume that viscous forces dominate the infiltration (non-wetting system) and that the flow preferentially fills the inter-tows macro channels. As seen in Figure 2.26, the bundles upstream are gradually saturated by a delayed secondary microflow, causing the total pressure to change. In this situation, capillary pressure will simply affect the time it takes to saturate the tows. Several studies recommended modeling permeability in terms of saturation or void content to improve accuracy [121,122].

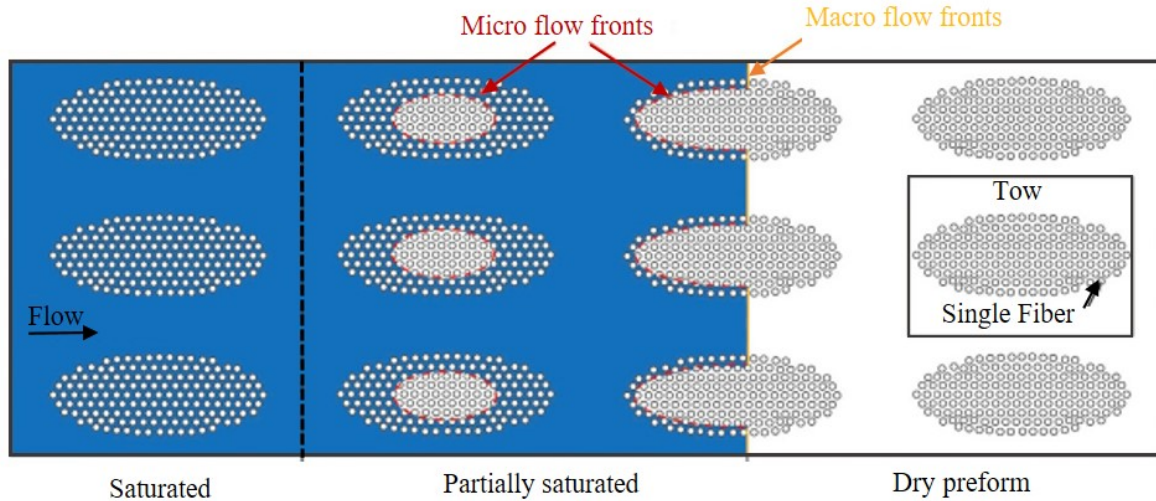


Figure 2.26 Representation of the dual phase impregnation schematic with micro and macro flow fronts [88].

Constitutive equations relating permeability, saturation, and capillary pressure are necessary for two-phase flow formulations. In order to determine k_r and s , several analytical parameterizations have been given, most of which follow a power law like the functional descriptions of Brooks and Corey (1964) and Van Genuchten (1980), among others [123,124]. Parametric investigations of virtual fibrous microstructures, as proposed by Ashari and Vahedi Tafreshi for thin fibrous sheets [125], can likewise be used to produce these formulations. Specifically for fiber reinforcements, Bréard et al. [126] presented a relative permeability rule based on

the ratio of unsaturated and saturated permeability.

The term *drainage* is used when a non-wetting fluid displaces a wetting fluid, whereas the term *imbibition* is used when a wetting fluid displaces a non-wetting fluid. Given the dynamic wetting circumstances during the impregnation, Nordlund et al. [117] used the semi-empirical expression derived by Van Genuchten and Mualem [127] used it to describe the impregnation of a glass preform by a resin. They demonstrated that modeling flow across a broader range of velocities may require several imbibition-drainage curves.

Similarly, Gascón et al. [119, 120] modeled the saturation in a glass fiber reinforcement to predict the void formation and transport processes using a formulation determined by Brooks and Corey [128]. Although a comparable degree of saturation might correspond to voids in the tows or in between, this method cannot a priori predict the spatial distribution of voids. Nevertheless, the reliance of the saturation curve on flow rate may be an indirect indicator of a change in void location.

The dual scale effects have also been taken into consideration in a number of publications that employ pre-existing flow simulation tools like liquid injection molding simulation (LIMS) [121, 122, 129, 130]. They are used as a representative model for wetting and non-wetting systems, the inter-regime transition, or for the prediction of average capillary pressure evolution between fibers. Finite element solvers are coupled with a level-set method for tracking the free surface and enriched for accounting for multiscale effects at the air-liquid-solid interface [131].

Particle-based solvers such as the lattice Boltzmann method, smoothed particle hydrodynamics (SPH), and moving particle semi-implicit (MPS) method have been used [132–134]. However, for the analysis of inter and intra-tow flow, MPS method is preferred for solving the incompressible flow analysis and boundary element techniques are another example of current interest in the employment of alternative numerical methodologies to account for the dual scale effects [135].

Patiño-Arcila and Vanegas-Jaramillo [136] examined the latest advancements in the use of the aforementioned techniques in modeling the dual-scale flow with a special emphasis on the incorporation of a new parameter as sink effect⁶.

The level set approach has been also used to simulate capillary-controlled displacements in porous media with nonzero contact angles. The defining characteristic of the method is a velocity that varies between the pore space and solid phase. This adds an additional component to the conventional level set equation such that, at a steady state, the contact

⁶This corresponds to the absorption of fluid in the tows on the macroscopic fluid-front positions.

angle is maintained on the solid phase while capillary and interfacial forces are balanced in the pore space.

We can observe from Figure 2.27 the ability of the model to mimic situations in which the contact angle is a function of location. The pore throat is surrounded by two discs having radii 10 times larger than the pore throat diameter, and the width of the pore throat is set to unity [137]. The flow front progression along the pore walls evolves slower when the contact angle is smaller at the edges, while for larger contact angles, the progression along the edges is larger. The flow front curvature can be seen elongating with the resistance offered by the edge with a smaller contact angle.

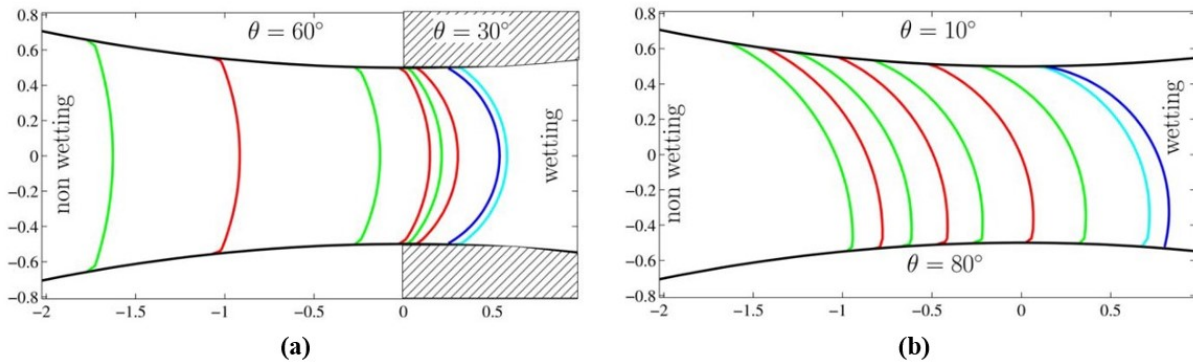


Figure 2.27 Two examples of pores, where the contact angle depends on the position. (a) Shows the change in the contact angle from 60° at the left part to 30° . (b) Shows the contact angle is 10° on the top pore wall and 80° on the bottom pore wall. The black lines represent the positions of the pore walls. The fluid interfaces are shown in alternate green and red colors with increasing curvatures. The last stable configuration is shown in cyan. Analytic results for the marginally stable interfaces are shown in blue color. The center of the pore throat is positioned at the origin in both figures [137].

Capillary imbibition in matrix with fibers

Preforms used in composite structures have highly anisotropic pore networks that range from micron-sized pores between fibers to millimeter-sized pores between fiber yarns woven or stitched together to make a textile preform. Due to the different methods of composite fabrication, including capillarity infiltration processes, and the considerable duration of fluid transition through the imbibition regimes, the capillary action in the complex poral network is combined with hydrodynamics and the rheology of the flowing polymer matrices [88]. Capillarity in CMCs becomes more accommodating of diverse phases with the effects of fluid interaction at the matrix fiber interface. Therefore, the complete dynamics of capillary imbibition can be most accurately modeled based on the representative volume element (RVE),

which comprises all the fundamental spatial singularities (pores, cracks, fiber-matrix interface, fiber-fiber interface). Due to the presence of different constituents, the imbibition hierarchy is based on the different scales of constituent phases.

In circumstances of extremely slow impregnation, with flow front speeds in the range of a few mm/min, micro-flow advances ahead of meso-flow, which results in the trapping of spherical voids between tows with sizes ranging from micrometers to millimeters. In a similar manner, high impregnation rates with typical flow front speeds in the range of several cm/min or higher result in a delay of impregnation of small spaces between fibers in tows, which in turn causes the formation of elliptically shaped, higher aspect ratio voids in the intra-tow spaces. This is because high impregnation rates delay the impregnation of small spaces between fibers in tows [105].

Using the Washburn and Richards equation to describe capillary imbibition makes the degree of saturation an important parameter that needs to be measured. The flow front progression, as seen from a two-dimensional viewpoint, presents two flow fronts, these flow fronts are macroscopic. The leading flow front is thinner than the one following it. This thinner diffuse flow front creates the necessary capillary bridge that imbibes the fluid without applying external pressure. In all likelihood, this variation of the flow front at the surface will also appear in a three-dimensional plane. The presence of micro- and macro-defects would also contribute to this overall capillary imbibition kinetics for a SiC matrix. The research context brings together all these aspects and develops a methodology to contribute to the imbibition dynamics and gradual evolution of porous network characterization with a visual reconstruction of the progressed flow front.

2.8 Research context

Many variables impact capillary imbibition in ceramic matrix composites at the MI stage, including the existence of pores, cracks, and fiber-matrix interphase. These parameters can either improve or impede fluid flow through the composite, resulting in changes in imbibition rate. Understanding the influence of these parameters on capillary imbibition is therefore critical for forecasting fluid flow rates through ceramic matrix composites.

Many methodologies are being used to study the impact of these elements. One option is to examine the flow of fluid through the composite using imaging techniques such as X-ray microtomography or scanning electron microscopy. These methods can offer precise information on the position and amount of matrix defects, as well as the shape of the fiber-matrix interphase.

Another technique is to replicate the capillary imbibition process in ceramic matrix composites using mathematical models. These models may account for the influence of defects and the fiber-matrix interphase on fluid flow and can give useful insights into imbibition mechanisms.

Moreover, flaws in the ceramic matrix, such as pores and cracks, can function as fluid flow barriers, resulting in slower imbibition rates. They can, however, operate as preferred fluid flow channels, resulting in quicker rates of imbibition. To effectively forecast the rate of fluid flow through ceramic matrix composites, it is critical to precisely quantify these flaws and their consequences on capillary imbibition.

Similarly, the fiber-matrix interphase can impact the imbibition rate by increasing or inhibiting fluid flow through the composite and fiber tows. This interphase is crucial in transmitting mechanical load between the fibers and the matrix and can have a major impact on the composite mechanical properties. Understanding its influence on capillary imbibition is therefore critical in forecasting fluid flow rates through ceramic matrix composites.

To summarize, the influence of pores, cracks, and fiber-matrix interphase on capillary imbibition at the MI stage in ceramic matrix composites is a critical element that must be considered in order to effectively forecast the rate of fluid flow and porosity filling. We can design more efficient and effective production procedures for ceramic matrix composites and increase their use in many applications by correctly defining these parameters.

CHAPTER 3 RESEARCH OVERVIEW AND OBJECTIVES

3.1 Overview

The industrial partner in the research project, Safran Ceramics, is involved in the development of processes to fabricate notably SiC/SiC CMCs that are used in high temperature applications such as in gas turbine engines. Because it is important to protect the CMC parts against environmental degradation in oxidizing atmospheres at high temperature, it is necessary to eliminate the open porosity in the material. This is why the melt infiltration (MI) step is inserted in the processing route of SiC/SiC CMCs.

The silicon melt infiltration process is used instead of sintering to make a dense component from a porous material body. The requirement is that the base material (SiC) be a porous body with a greater melting point than the invading liquid substance (Si). In addition, the melt must wet the porous material to generate capillary flow. Capillary forces pull the melt through the pores of the body, entirely filling the pore volume [138].

This process allows for the creation of microstructures that would otherwise be impossible to create by sintering. Before melt penetration, reactive components, such as carbon for example, can be injected into porous bodies. New phases are produced during infiltration as a result of chemical reactions with the melt. The reaction between carbon and the molten silicon during infiltration, creates more silicon carbide and considerably improves the hardness and stiffness of the Si–SiC material [138].

It is absolutely necessary to have an understanding of the infiltration processes that take place during the MI process in order to improve the product quality, as well as the efficiency with which the process uses energy and resources. Unfortunately, because of the high process temperature for silicon MI, which is over the silicon melting point of 1410 °C [139], performing the essential research proves to be complicated.

The scope of the present study proposes the creation of a comprehensive approach for characterizing capillary imbibition dynamics based on pore scales and shape. The experimental approach is confined to ambient temperature infiltration to simulate MI process, excluding then chemical reactions at high temperatures. Some important parameters have been found as the basis for selecting a model fluid. Surface tension, viscosity at room temperature, wettability, and density are all variables to consider. The schematic for this approach is shown in Figure 3.1.

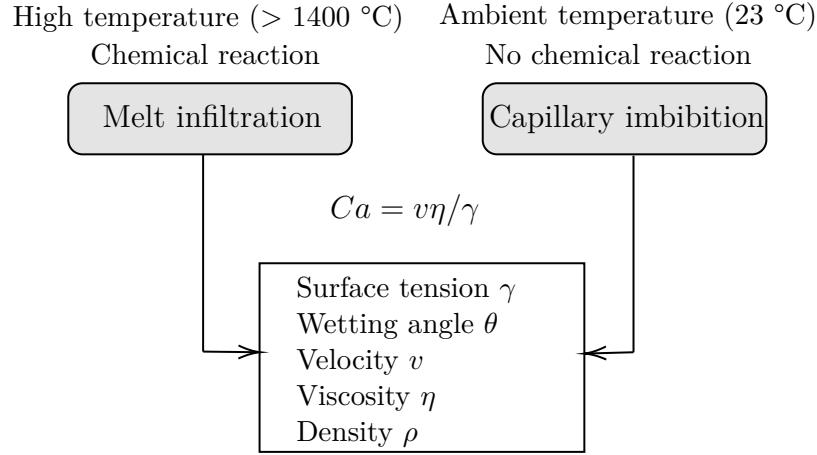


Figure 3.1 Schematic of the dimensional analysis approach to determine the characteristics fit for a model fluid at ambient temperature to simulate the MI process excluding effects of high-temperature chemical reaction.

Capillary number Ca combines imbibition velocity v with viscosity η and surface tension γ , as expressed by the formula given in Figure 3.1. As a result, fluids with the same order of capillary number will exhibit similar imbibition dynamics, and an analytical bridge between imbibition dynamics at high and room temperatures could be built. The dimensionless capillary number was used to compare a variety of prospective alternatives for model fluid. Table 3.1 gives the properties of the fluids selected for the present study, *exo*-DCPD having similar properties as hexadecane. If it is quite easy to evaluate the viscosity and surface tension of a fluid at a given temperature, it becomes less obvious to evaluate the characteristic velocity v of that fluid since it is a physical response of the system to flow conditions and not a fluid property. Nevertheless, preliminary experiments were carried out to evaluate the order of magnitude of the characteristic velocity v for the fluid of interest; these values are given in Table 3.1. For liquids having a capillary number $Ca < 10^{-5}$, the flow in porous media is dominated by the capillary forces.

Fluid	Temperature ($^{\circ}\text{C}$)	Surface tension γ (N/m)	Viscosity η ($\text{Pa}\cdot\text{s}$)	Velocity v (m/s)	Ca ($-$)
<i>exo</i> -DCPD	20	0.024	2.3×10^{-3}	10^{-5}	1.2×10^{-6}
Hexadecane	20	0.027	3.0×10^{-3}	10^{-5}	1.1×10^{-6}
Silicon	1415	0.86	9.4×10^{-4}	3×10^{-4}	3.3×10^{-7}

Table 3.1 Comparison of fluid properties to establish the model fluid at ambient temperature for SiC.

Even if the capillary number Ca for hexadecane and liquid silicon is not of the same order of magnitude, their values are still low enough to consider the dominance of capillary forces. The selection of hexadecane as model fluid is also based on its non-volatility and on its very good wetting (contact angle $\theta = 0^\circ$) on SiC. It was used in impregnation studies, which allowed us to define the macroscopic scale of the poral network of the granular and porous environments.

3.2 Objectives

The SiC/SiC CMCs developed in the context of the research project with Safran Ceramics consisted of 3D SiC fiber preforms infiltrated at the slurry cast step by SiC fine granular matrix. Since the fiber preforms are subjected to CVI processing step, the resulting coating tends to close the fiber tows blocking then the access to the capillary fluid. So in MI process, it is primarily the porosity of the granular matrix that drives the capillary flow. Nevertheless, the processing variables at the SC step leads to various scales of pores and defects in the granular matrix: micro and macro-pores, and cracks. This is the reason why the experimental works in the present study are focused on the simulation of different porosity features in the porous granular matrix.

Characterization of a porous SiC matrix would include all essential factors that have substantial effects on imbibition dynamics. To observe the imbibition phenomena, the characterization process must be representative of the interactions of multiple factors at the macro scale. A better understanding of imbibition dynamics would aid in the development of different strategies in selecting the capillary paths associated with melt infiltration process for the production of MI-CMC components for high-temperature and integrity applications.

The main objective of the research project is to better understand the physical mechanisms occurring during capillary flow in porous granular SiC matrix containing different poral network characteristics. This main objective can be broken down into the following specific objectives (SO):

- **SO1:** Evaluate the impact of microstructural features (pore size and shape, porosity level, microcracks, heterogeneous distribution of porosity) on the capillary imbibition of porous SiC granular matrix specimens with the aide of controlled capillary rise experiments.
- **SO2:** Characterize the front flow interface by means of interrupted impregnation flow. This includes the development of an approach for the capillary rise experiments and the characterization of the degree of saturation of the interface.

- **SO3:** Verify and validate the progression of capillary flow in 2D specimens from the numerical simulation of unsaturated flow based on the Richards equation. Determine the limitations of this calculation approach by considering the saturation profile, the presence of defects in the pore network, the characteristics of porous materials (porosity, median pore size, tortuosity), etc.
- **SO4:** Characterize the imbibition hierarchy in heterogeneous porous media to describe the phenomenological sequence of events during the capillary rise in a porous granular SiC matrix.

The current research endeavour pertains to the examination of capillary imbibition within the granular matrix phase typical of a CMC. An industrial CMC is composed of diverse scales and classifications of voids that take on various spatial manifestations. A significant endeavour has been made to incorporate spatial singularities by examining the interplay of imbibed fluid across various void scales within the matrix. The proposed microstructural analysis template, which incorporates imbibition quantification, is applicable to the capillary imbibition analysis of a CMC. The ceramic matrix composite (CMC) exhibits a relatively homogeneous dispersion of its constituent phases, namely the fibre and matrix, resulting in a notable level of microstructural symmetry in its properties (thermal, mechanical, electrical). The utilization of a granular matrix signifies a spatial distribution of voids that is more randomized in nature. This approach is considered to be more complex than a simplistic one and can be applied to the analysis of CMC at an industrial scale.

If these objectives are reached, it will be possible to have a deeper understanding of the phenomenon as a whole, not only on different scales but also at high temperatures. This would open the door to new process approaches for upgrading the existing MI-CMC manufacturing technique into one that is more efficient and cost-effective. This might lead to the democratization of technology that is extremely end-use specialized. As a component of the comprehensive characterization, the pore shape would be defined in the flow hierarchy as well as the preferred imbibition scenarios. It is essential to do a flow front analysis in order to demonstrate the existence of two distinct diffuse-type flow fronts, which are produced by different visualizations (2D and 3D). The proposed objectives span over five distinct phases (to be described in the next Chapter), which, when combined, produce an all-encompassing structure for effective imbibition characterization.

CHAPTER 4 EXPERIMENTAL METHODS

This chapter gives a description of the experimental methods for the development of the different configurations of specimens to achieve the proposed objectives of the research. The overall project domain is divided into five phases that are categorized based on the geometrical and microstructural features of the specimens such as thickness, poral network, and geometrical variations. The first two phases set the production of granular SiC matrix specimens with simple geometry and proportions. Geometrical complexity is gradually introduced by varying granular dispersion. The degree of saturation at the surface and the interior of the sample volume, as well as corner imbibition with the growth of the diffuse flow front at the surface, have been emphasized for the analysis of capillary flow.

The final phase (V) incorporates macro defects in the matrix to reproduce multiphase imbibition through porous media that are typical of the matrix of SiC/SiC CMCs. The experimental portion of this phase V has been completed by Floriane Dewart as part of her master's thesis [140]. The experimental results she obtained will not be given in detail in the present thesis but some elements of the results will be considered in the analysis of capillary flows. As shown previously in Figure 2.12, typical microstructure of SiC/SiC CMC contains various pore and cracks features that explain the complexity of the analysis of capillary mechanisms. The selection of the five phases aims to isolate some features that could be encountered in the granular matrix of CMC: characteristics of porous media (phases I and II), variability in the flow section (phase III), heterogeneity of pore network (phases III and IV) and macro pores and cracks (phase V). This will be described in the following sections.

4.1 Planning of experiments

The experimental characterization of porous media and capillary flows has been divided into five separate phases. These phases, from I to V, are schematized in Figure 4.1 illustrating the main parameters in terms of geometry and granular matrix formulation. The three slurry formulations referring to letters A, B and C in Figure 4.1 permit to obtain different pore network characteristics, which is one important variable to study in order to meet objective SO1. The description of these three slurry formulations will be given in Section 4.2.1.

By modifying the slurry formulation, phase I creates the simplest geometry with the poral network as the variable. The second phase keeps the same slurry formulation but imposes variations in the thickness of samples. The third phase introduces geometrical complexity in the form of hollow geometry that forces the capillary flow to divide its path into two

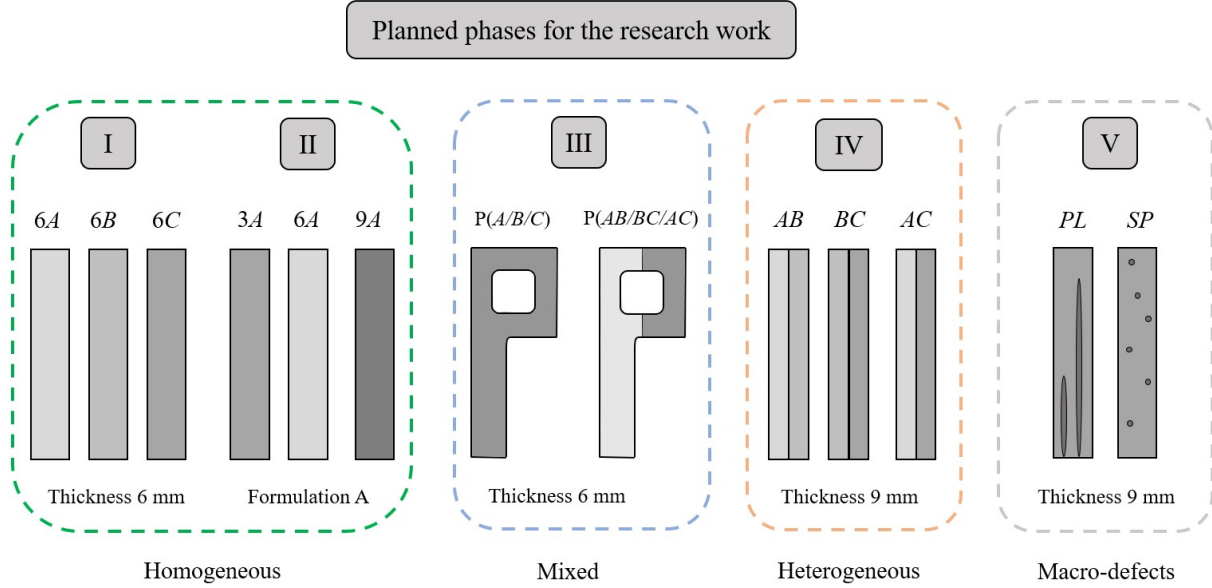


Figure 4.1 The planned five phases for the fabrication of porous matrix with a geometrical variation. For phases I and II, the designation numbers 3, 6, and 9 refer to the thickness (in mm) of the specimens. For phases I to IV, the letters *A*, *B*, and *C* refer to the slurry formulations. For phase III, the letter *P* refers to P-shaped specimens. For phase V, *PL* refers to planar defects (simulating cracks) and *SP* refers to spherical macro pores.

separate branches. A degree of complexity was also added to the poral network by producing samples with heterogeneous structures. The fourth phase with heterogeneous structures was fabricated from two slurry formulations in the same sample to simulate interface effects in imbibition. The fifth phase has spherical and planar voids inserted as macro-defects. Overall, the study aims to achieve a better understanding of capillary imbibition (specific objective SO1) by exploring the flow front and the saturation gradient near the surface and in the center of the specimens (SO2). The study aims also to gain insight into capillary flow dynamics and how they are affected by variations in porosity, geometry and degree of saturation. Therefore, this study could help to develop more effective and efficient manufacturing process for ceramic materials with specific poral network.

The geometric dimensions were determined by taking into account the potential size of the high-temperature oven utilized in the heat treatment process. The heat treatment has a significant influence on the ensuing poral network due to the amalgamation of the granular phase, which generates complementary voids. The details about heat treatment of specimens will be presented in Section 4.2.3. The typical dimensions of the specimens are shown in Figure 4.2, while more variance in size may be noted during the actual manufacture of the specimens.

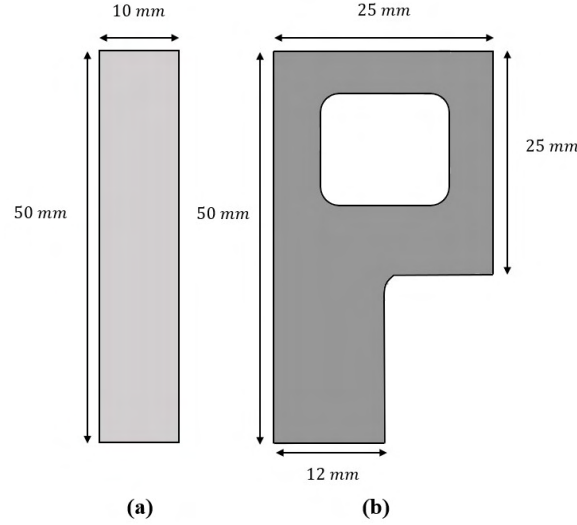


Figure 4.2 The dimensions for the two typical geometries which have been incorporated in this study evolves from (a) simple rectangular (phases I, II, IV and V) to (b) complex P-shape with the inclusion of heterogeneity (phase III) and interface imbibition dynamics.

The injection technique for both geometries shown in Figure 4.2 is identical except for the necessary changes made in the mask that generates the mold contour for slurry casting. There are also some variations in the injection approach used between homogeneous and heterogeneous specimens. The injection did not offer a substantial challenge for homogeneous specimens. With heterogeneous specimens, however, the method evolved into a more sophisticated process. The final injection settings were carefully determined to achieve control of the poral network. The detailed procedure for the production of slurry cast specimens will be presented in Section 4.2.2.

4.1.1 Phase I: Homogeneous specimens with different poral networks

In the first phase, three distinct porous networks are created based on the granular compaction of each particular slurry formulation since granular compaction and porosity are correlated. The three different poral networks that correspond to three slurry formulations are designated by the letters A, B, and C as shown in Figure 4.3.

The same SiC powder batch was used to prepare slurries of types A and B; only the method for preparing the slurries is different. This leads to low compaction for specimen B (high porosity level) and high compaction for specimens A (low porosity level). Specimens C were prepared from a completely different SiC particle formulation; it will have the highest granular compaction, resulting in the lowest porosity of the three varieties. The proportion of the powder phase within the volume of the specimen dictates the porosity level and the

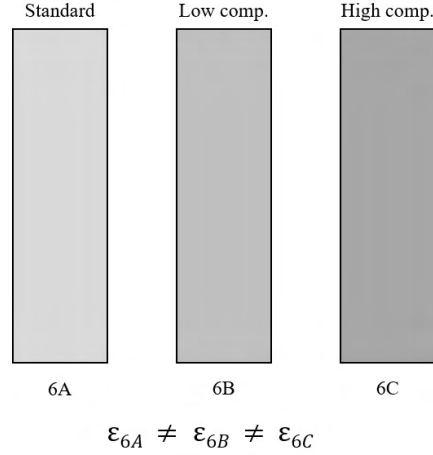


Figure 4.3 Phase I rectangular specimens that include different compaction that would correspond to different porosity levels for each slurry formulation. Porosity level and median pore size will be the basic parameters of the poral network for this phase.

pore size distribution of the final granular phase.

4.1.2 Phase II: Homogeneous specimens with different thickness

During this phase, samples with different thicknesses (3, 6 and 9 mm) will be fabricate to study the effect of this parameter on capillary imbibition. The schematic of the specimen geometry for this phase is presented in Figure 4.4. Slurry of type A was selected as the single formulation for this phase. The experiments of this second phase would shed light on the influence of the dispersion of granular media when the consolidated volume (or thickness) is decreased.

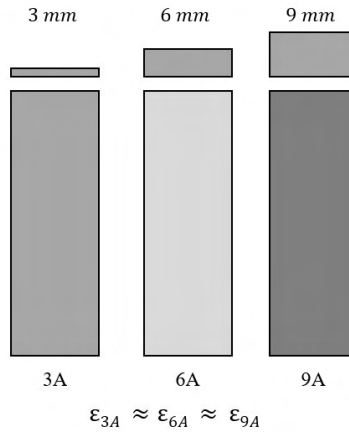


Figure 4.4 Rectangular specimens for phase II with varying thickness.

The purpose of this study is to find the effect of changing specimen thickness. At the pore scale, the resultant poral network is determined by the method of consolidation of the granular SiC particles; the pores or voids serve as the complementary phase to the solid phase. If the behavior of capillary flow is influenced by the thickness of the specimen, it would provide useful information in the design of the capillary path to impregnate SiC/SiC CMC parts with complex shapes.

4.1.3 Phase III: Homogeneous and heterogeneous specimens with complex geometry

Prior to phase III, change was restricted to geometrical (thickness) and dispersion parameters (slurry formulation). In phase III, a combination of geometrical complexity and slurry formulation variation in the same specimen configuration (heterogeneous) is studied. In terms of morphological effect at corners and interface between the two formulations, this includes additional imbibition situations that are interesting to characterize and analyze the capillary flow behavior.

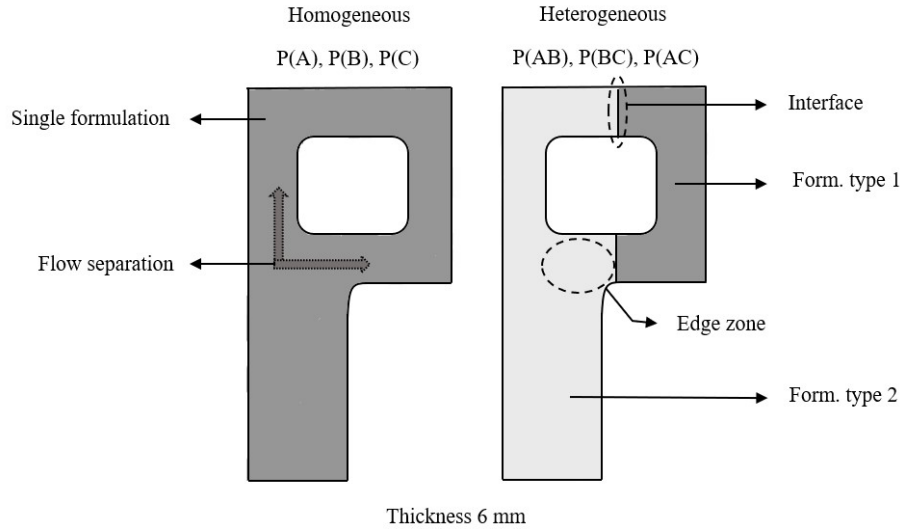


Figure 4.5 P shape specimens for phase III with complex divergent-convergent sections and corner sections in homogeneous and heterogeneous configurations. Letter P in the designation refers to P shape geometry of the specimen. Letters A, B and C for homogeneous specimens refer to the slurry type. For heterogeneous specimens, the letters AB, BC and AC refer to the combination of slurry types in a specimen.

As shown in Figure 4.5, the two subdomains of this phase consist of homogeneous and heterogeneous specimens, respectively. In the designation of these specimens, The letter P refers to the P-shape geometry. For homogeneous specimens, slurries of type A, B and C

were characterized. For heterogeneous specimens, the designation contains the letters of the two slurry formulations (AB, BC and AC) that are separated by an interface as shown in Figure 4.5.

For capillary imbibition tests, the fluid enter at the base of the P shape specimens and progress vertically towards the loop of the P. At this point, the fluid flow is divided into two branches following curved corners. Also, when the specimens consist of two distinct poral networks that are linked to form an interface between them, the kinetics of interface diffusion will play an important role in flow hierarchy (SO4) in heterogeneous porous media. In this case, the fluid flow direction is perpendicular to the interface between the two pore networks.

4.1.4 Phase IV: Heterogeneous bi-laminar specimens

In phase IV, the configuration is heterogeneous with a uniform cross-section. The role of the interface between the two consolidated formulations is emphasized in this phase. The typical description of specimens for phase IV is shown in Figure 4.6. The bi-laminar specimens are fabricated by casting two different slurry formulations side by side. For this specimen geometry, the fluid flow direction is parallel to the interface separating the two formulations. Since the compactness of granular media determines the level of porosity of each formulation, the first step in classifying porous networks was to control the compactness parameters during the slurry-cast stage at room temperature to get the desired porosity.

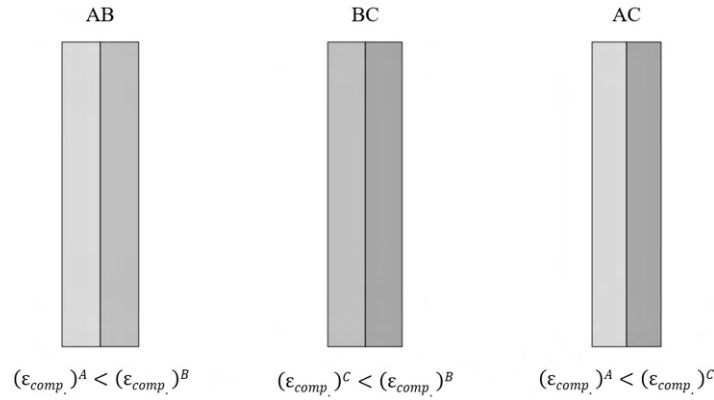


Figure 4.6 Bi-laminar specimens of phase IV with two different microstructures with similar overall thickness of 9 mm. Letters AB, BC and AC refer to the slurry formulations that were used to produce the specimens.

The comparative flow front evolution between two interconnected poral networks could also provide a better comprehension of the transition behavior of model fluid in a porous matrix (SO2, SO4).

If a macro crack runs through the interface, it could generate the edge effect in imbibition, which also induces a hierarchy of flow (SO4). The fluctuation in the degree of saturation between the surface and volume would also be useful to quantify the capillary flow in distinct pores scales as it could influence the flow hierarchy for porous SiC matrix.

4.1.5 Phase V: Effect of induced defects in SiC matrix

The objective of this phase is to visualize and quantify the effect of induced defects on the imbibition kinetics of porous SiC. The goal is to investigate the capillary processes that occur near defects in a SiC matrix so that preferred impregnation routes may be predicted and residual porosity in CMCs avoided. Porosity must be managed by four criteria: size (must fall within the range specified by Safran Ceramics), shape (spherical or planar), macro porosity level (5 or 10 vol.%), and spatial distribution (homogeneous) [140]. Due to the different scales of porosity present in the raw material, it is important to measure and identify the flow hierarchy based on the different imbibition dynamics in the defects based on the capillary rise kinetics (microscopic and macroscopic scale) associated with the respective microstructures.

Figure 4.7 depicts the microstructures required for materials with spherical and planar defects. The utilization of both spherical and planar flaws provides useful information to understand the capillary flow behavior in real CMC porous materials. Spherical flaws can provide localized areas where macro pore surface curvature can cause the arrest of flow front around the defect, thus influencing the capillary pressure and flow behavior. Planar flaws, on the other hand, might generate bigger continuous channels for the fluid to progress through, affecting the imbibition kinetics. Intergranular porosity refers to the small voids that exist between individual ceramic grains. The purposeful introduction of flaws creates macroscopic porosity [140].

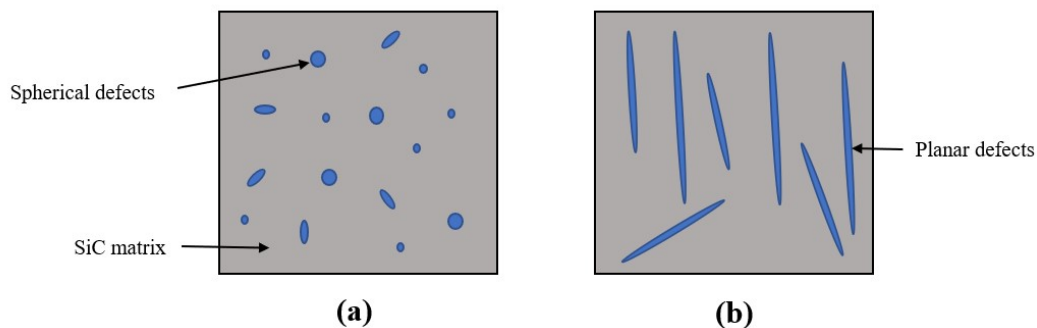


Figure 4.7 The two types of induced defects in rectangular SiC matrix with uniform thickness: (a) spherical macro pores and (b) planar defects simulating cracks.

Since most of the information concerning this section was developed in the master thesis of Floriane Dewart, a general overview will be treated in the discussion section of the present thesis.

4.2 Fabrication of SiC matrix specimens

The fabrication of SiC matrix specimens requires careful control over process parameters. The process begins with the mixing of constituents that make up the slurry mixture. They include SiC powder with a water-based binder mixture with varying proportions of granular phase which determines the extent of compaction of the SiC matrix.

The protocol for slurry preparation is pre-defined by Safran, and the final slurry has to be validated against the reference parameters to be able to proceed with the SC equivalent injection process. The protocol and reference parameters are proprietary information and cannot be disclosed for public documents. The schematic of the fabrication of SiC matrix specimens is presented in Figure 4.8.

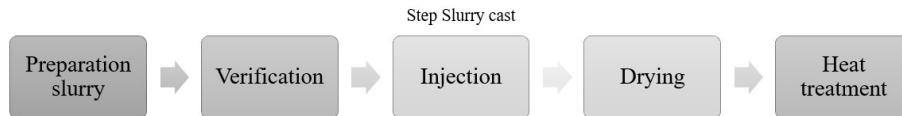


Figure 4.8 The steps incorporated in the manufacturing of SiC matrix specimens for pre-scribed phases; each process step has to be controlled to obtain the desired poral network.

The verification of the prepared slurry is followed by the injection process, and the process parameters are finalized depending on the final design requirements. The mold has been kept the same, and variations in PTFE masks to produce different shapes were introduced that save resources and time. The fabrication process includes the steps from mixing powder to heat treatment.

4.2.1 Preparation and validation of the slurry

Slurry preparation begins with the dispersant being mixed into the base fluid. A binder is added that acts as a cementing agent between the granules. The standard, high, and low compaction slurries are determined by the different proportions used to create the three types described in previous sections. The duration of mixing determines the degree of dispersant needed to reduce particle agglomeration.

Before injection, the prepared slurry is passed through a validation process that determines if it is fit for injection. To maintain the uniformity of the granular phase, additional ultrasonic

agitation is carried out for a specific duration. Just before injection, the slurry formulation has to be maintained within the prescribed pH limits.

As a technique of slurry validation, Safran Ceramics employs the characterization of the slurry rheology to guarantee that it can be injected with the employed injection system. A rheometer (Anton Paar, MCR501) measures the viscosity of the slurry. It imposes a constraint (shear) on the examined slurry, allowing the viscoelastic characteristics and flow of the suspension to be studied.

The measuring cell (Anton Paar, C-CC27/T200) features a straightforward Couette geometry composed of coaxial smooth cylinders. This geometry is utilized for liquids with low viscosity. The slurry is given a shear rate of 300 s^{-1} , followed by a 2-minute rest time. The viscosity measurements are then conducted between 300 s^{-1} and 0.1 s^{-1} . Lastly, measurements of viscosity between 0.1 s^{-1} and 300 s^{-1} are conducted.

Many industrially important fluids, particularly multiphase substances such as emulsions, dispersions, and suspensions, slurries, for example, polymeric melts and solutions (natural and synthetic), do not conform to the Newtonian postulate of the linear relationship between shear stress (τ) and shear rate ($\dot{\gamma}$). So, we also call these fluids non-Newtonian, non-linear, and rheologically complex [141]. This character of the fluid would induce dispersion in the consolidated porous matrix based on non-Newtonian behaviour of the slurry mixture.

Type	Concentration	pH range	Identification
A	20 % vol.	10 - 10.5	Standard compaction (SC)
B	20 % vol.	10 - 10.5	Low compaction (LC)
C	35 % vol.	9 - 10	High compaction (HC)

Table 4.1 Range of powder concentration with acceptable pH range for the fundamental formulations that form the basis of all coming configurations.

The typical size of silicon carbide particles ranges between 90 and 3310 nm [142]. The degree of agglomeration and pH correction determines the final porosity and pore network. The creation of a porous SiC matrix is due partly to the dispersion of the slurry constituents; the relative concentrations for each formulation have been supplied as a reference for the investigation of granular phase dispersion in the mixture.

4.2.2 Injection of slurry: slurry cast

The injection of slurry corresponds to the slurry cast method in the fabrication of SiC/SiC CMCs. In this stage, a mixture of SiC powder and other necessary additives, and binders is injected under constant pressure for longer durations of time. This constant pressure allows

the particulate phase to consolidate, and the residual suspension base fluid is released through filtration. The wet, consolidated matrix is then dried under ambient humid conditions, and the specimens are ready for post-drying heat treatment. This is a very significant stage since the geometrical integrity and tolerance depend on the degree of sealing in the mold and the careful de-molding of samples with minimum destruction to the wet consolidated matrix.

The exploded view of the mold (Figure 4.9) shows the orientation of different individual plates that combine to form a closed chamber. The top plate has three injection ports that are interchangeable. The middle plate has a cavity that houses the assembly of Polytetrafluoroethylene (PTFE) masks defining the contour of the specimens.

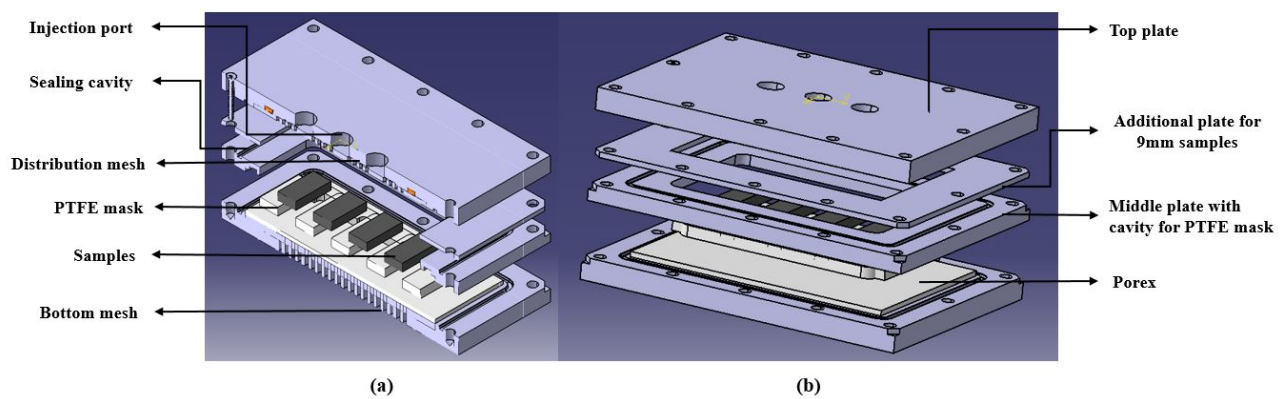


Figure 4.9 The exploded view of the designed mold for the fabrication of SiC matrix specimens by slurry cast. The PTFE mask (white) is modified as per subsequent design requirements for phases III and IV. After the slurry is injected through the ports on the top of the mold, it is filtrated through Porex filter to retain SiC particles in the mold cavity.

The pressure gun assembly that was used for injecting the slurry in the mold is presented in Figure 4.10. Another view of the whole injection system and the mold is shown in Figure 4.11. The slurry is moved in a polypropylene tube (b) that has a steel casing around it (a). This steel casing is connected to the pressure gun (c). During the injection process, the gun assembly is attached to a support to keep it steady. It is important to seal all the seams to ensure that slurry does not leak out since the loss of pressure and slurry drastically affects the slurry cast process. The continuous injection for homogeneous samples has been described with a visual representation of the complete setup, Figure 4.11.



Figure 4.10 The pressure gun assembly with the attachment to the mold with the transfer pipe through one of the three injection ports [140]. (a) Steel casing; (b) polypropylene tube; (c) pressure gun; (d) tygon tube.

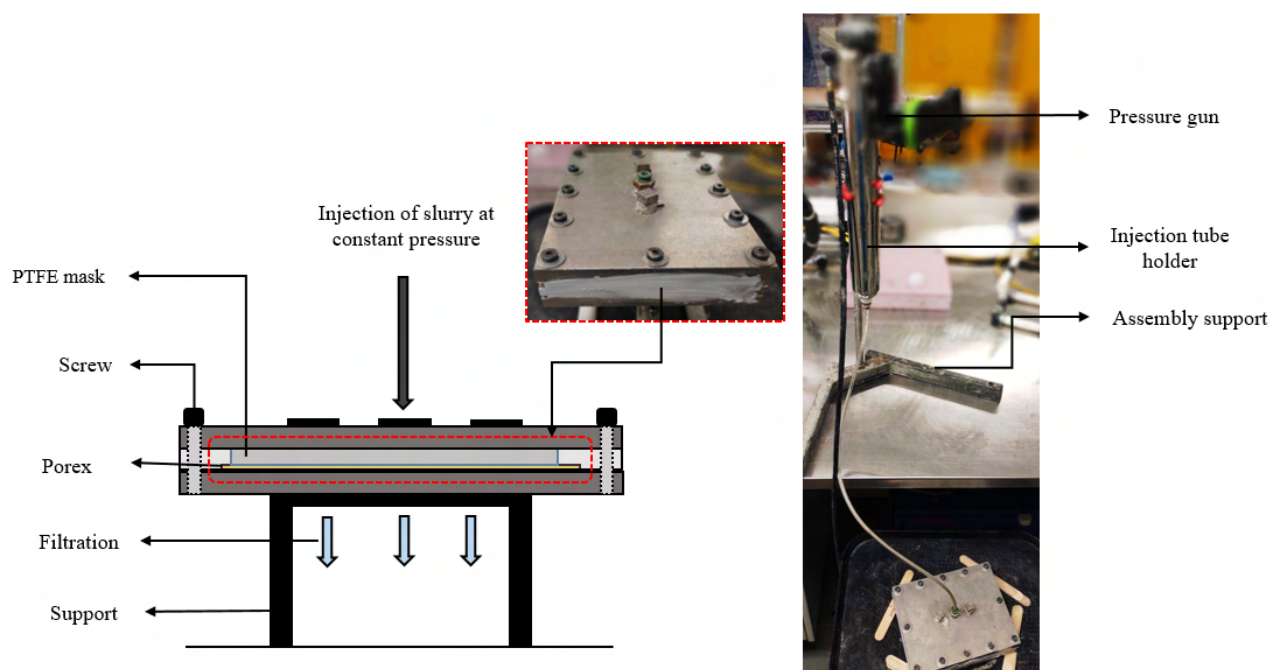


Figure 4.11 Assembly of mold and injection system for producing granular SiC specimens, the setup is similar for continuous and interrupted injection strategy.

In the continuous injection of homogeneous samples, the mold is sealed once the injection commences, and it is opened only at the end of the complete consolidation process; this consolidation duration includes the injection duration. This duration has been tabulated along with the corresponding pressure values for each formulation. The values prescribed in

Table 4.2 reflect the optimum duration so as not to cause any breakage during handling and manipulation. The injection should not be done for longer durations to avoid over-drying of samples that result in generation of transverse and longitudinal cracks. After filtration of the slurry by the porous PTFE filter (Porex) that retains the particulate phase and releases all the residual liquid, the slurry forms a packed granular solid, named *cake*. The consolidation of the granular solid occurs under the application of constant pressure. The duration of applied pressure (given in Table 4.2) is also significant for obtaining the best consistency for the sample.

Slurry type	Pressure (bar)	Injection time	Drying time (hrs)
A	2.4 - 2.7	35 - 50 min	10 - 12
B	2.4 - 2.7	30 - 40 min	10 - 12
C	2.4 - 2.7	24 - 30 hrs	15 - 20

Table 4.2 Injection parameters that include the duration for consolidation (inside the mold) and drying in the ambient environment. The resulting samples are highly fragile and thus need to be heat treated to obtain the requisite three different poral networks.

The pressure and drying conditions are kept the same, but an interrupted injection strategy is employed for the fabrication of heterogeneous specimens; a detailed explanation will be provided in the next subsection. The de-molding of the consolidated SiC matrix also becomes challenging and necessitates more stringent process control and handling of specimens so as not to destroy them.

PTFE was chosen to fabricate the masks for a number of properties such as the material being chemical resistant, non-sticky with low friction, and non-wetting. These characteristics are necessary for the efficient injection of the slurry with the least wastage of resources. The edges of the plates have o-ring grooves for hermetic sealing and the top plate has screws that complete the assembled mold ready for injection.

For each phase, only the mask design was changed without making any discernible modifications to the steel outer shell components except the addition of an additional plate for the fabrication of 9 mm samples. Emphasis was also given to making the most use of the injection volume to maximize the sample output injection per cycle. The respective specimens that can be prepared per injection cycle are presented in Figure 4.12, along with the mask designs for individual phases.

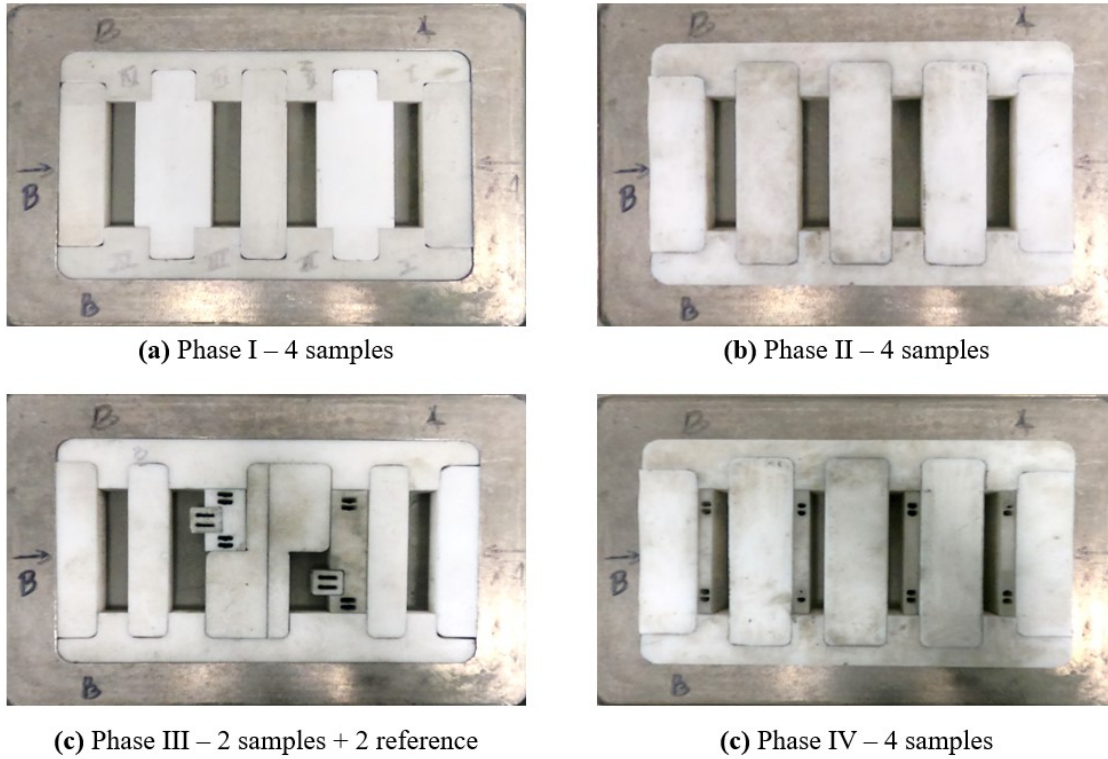


Figure 4.12 Different configurations of PTFE masks for the consolidation of porous SiC matrix. The maximum number of specimens that can be obtained per injection is also provided for each phase.

The masks for the first two phases with homogeneous formulations are simple rectangular geometries. However, for phase III which includes the complex P-shape geometry, the design was modified (shown in Figure 4.13) to accommodate a central cavity of 10 mm $\times$ 10 mm. The inclusion of an additional cavity for phase III brings additional modifications to the mask design and the overall injection protocol.

For the samples of phase IV that have bi-laminar configuration, there are major changes in the injection protocol while there is no modification to the mask except the addition of a support plate to increase the thickness by 3 mm. The detailed utility of the mask inserts will be discussed when the injection strategy for these phases will be described in the next subsection.

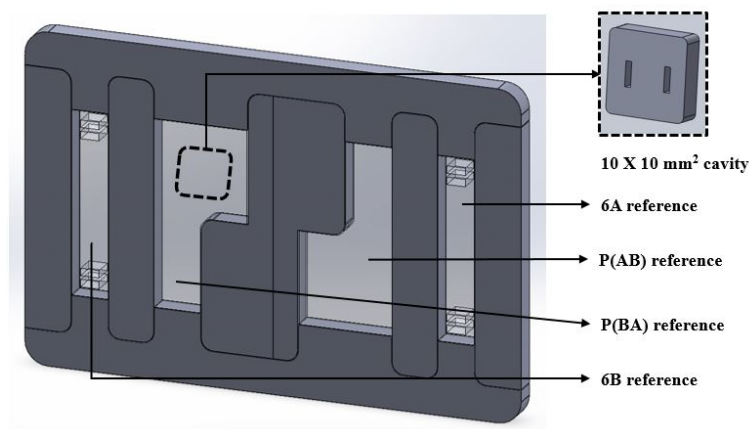


Figure 4.13 Modified PTFE mask for phase III for both heterogeneous and homogeneous specimens. An additional reference cavity was introduced to permit the characterization of the poral network reference on either edge.

Modified strategy for heterogeneous specimens of phases III and IV

The injection protocol for the fabrication of heterogeneous specimens is not continuous. There is a specific sequence for the injection that commences with the injection of the first slurry; this first round includes either A or B-type slurry. This is done so that there is sufficient time for slurry A or B to consolidate so that the next slurry can be injected. Since the C-type formulation requires a considerably longer drying duration (both inside and outside the mold), this is always injected after the first slurry is consolidated.

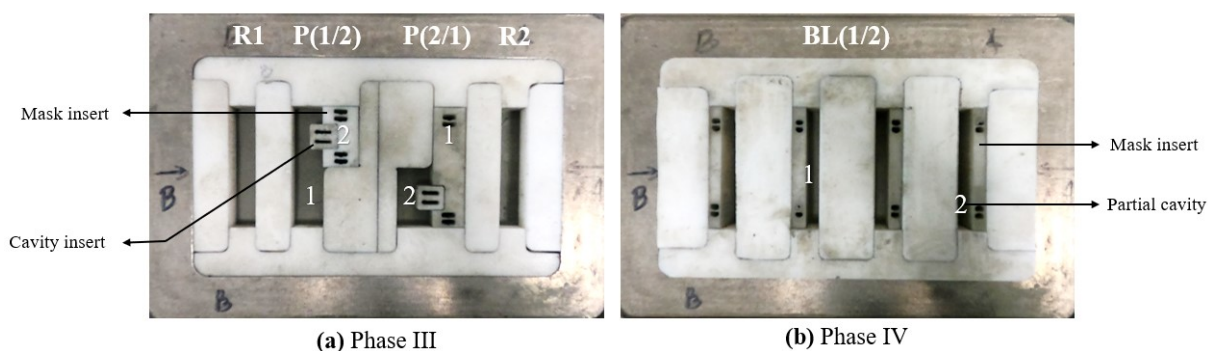


Figure 4.14 Modifications in PTFE masks for interrupted injection strategy in phases III and IV to fabricate heterogeneous specimens.

This requires opening the mold to remove the additional mask inserts. The mold is cleaned and re-sealed for the second round of injection. The mold orientation (horizontal) for the interrupted injection is similar to the one used for homogeneous specimens. The details for

PTFE masks for this modified approach for interrupted injection is shown in Figure 4.14.

Due to the procedure for changing the slurry mid-injection, the overall duration for the injection of heterogeneous specimens is longer as compared to homogeneous specimens. It has to be ensured that there is no leakage during the changing of the slurry. The de-molding for heterogeneous specimens is also challenging since there is a central cavity that reduces the structural integrity of the SiC-consolidated matrix. A parallel injection setup was designed for the injection of two slurries consecutively; however, this parallel setup would not be efficient if there was a need to re-open the mold after half the injection. Therefore, a single injection strategy was employed to obtain the consolidated heterogeneous specimens. The horizontal orientation of the mold facilitates the filtration of the suspension with gravity. The schematic of the orientation of the mold and injection was presented in Figure 4.11 to better understand the consequences of choosing this configuration.

4.2.3 Heat treatment of consolidated SiC specimens

Heat treatment under controlled conditions is the next step in making matrix specimens. This process is significant in the generation of the final porous network because of the conditions under which heat treatment occurs. The oven used for high-temperature heat treatment is the RD-WebbTM model G. The heat treatment is performed to have the maximum possible quantity of specimens in the chamber without compromising on the process parameters. Some of the main technical specifications for the RD-Webb oven are given in Table 4.3. The complete heat treatment process time includes the duration for heating and cooling the chamber as shown in Figure 4.15.

Technical specifications for the RD-Webb TM type G oven	
Maximum temperature	2000 °C with vacuum
Ultimate vacuum with turbo	10 ⁻⁶ mbar
Work zone	90 mm dia × 50 mm tall
Insulation	Graphite
Heating element	carbon-carbon

Table 4.3 Specifications of the oven used for the heat treatment of the fabricated SiC porous specimens [143].

The heat treatment is performed under vacuum, and the cycle is initiated only when the vacuum with the turbopump attains a value inferior to 10⁻³ mbar. The uniformity of the poral network in fabricated specimens after heat treatment has to be validated by comparing the loss of mass during the heat treatment.

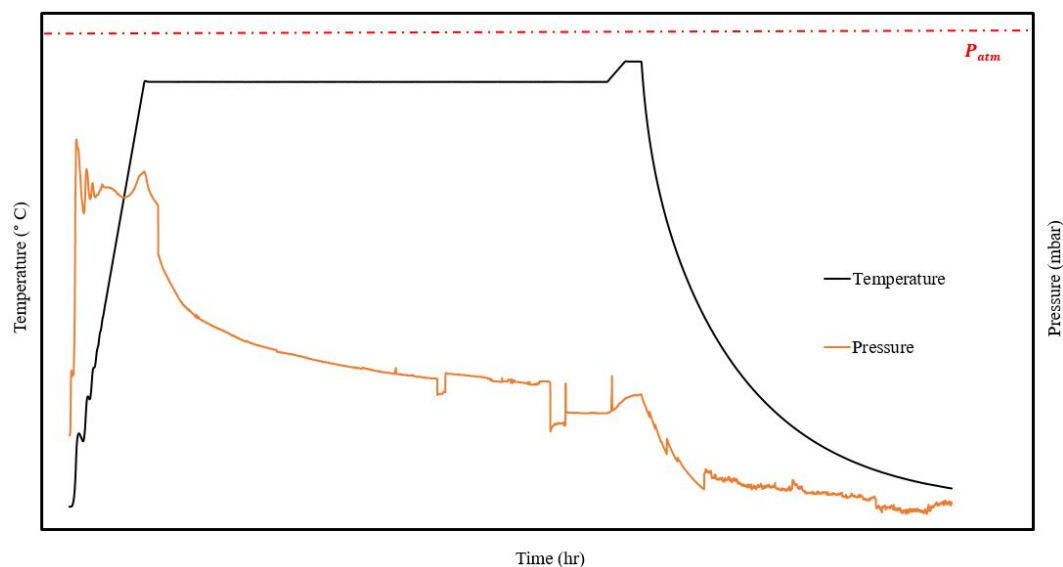


Figure 4.15 The typical heat treatment cycle utilised as a part of the fabrication procedure for SiC matrix specimen.

This step ensures the progression of specimens that are fit to be used for further analysis (have the least dispersion of the poral network). The loss of mass is due to the combustion of a binding agent which is an additive for the three formulations. Since each batch produces four specimens for phase I and II, the comparison has been presented for the two batches (B01, B02) in the same formulation (A/B/C). As shown in Figure 4.16, the dispersion in mass loss on specimens taken from one batch to another is quite low, indicating uniform combustion of the binder in the first part of heat treatment.

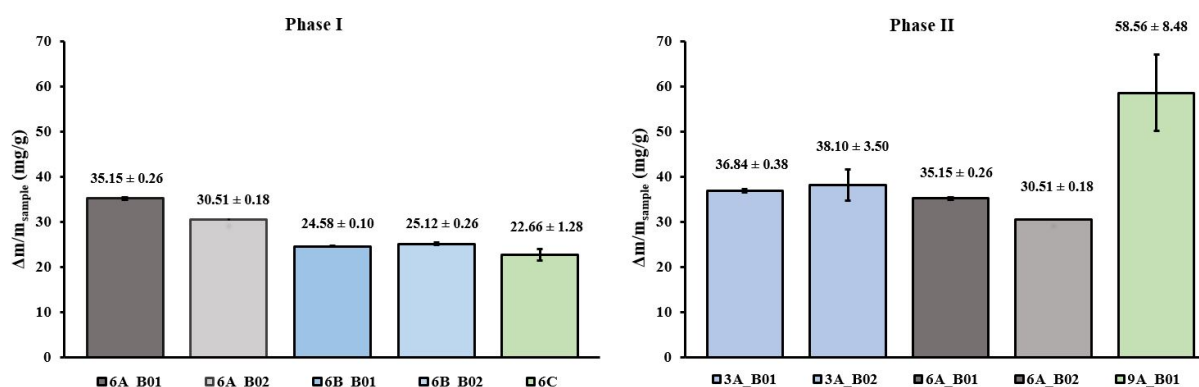


Figure 4.16 The comparison of mass loss after heat treatment provides the initial validation of the uniformity in the resulting microstructure. The dispersion in mass loss between the samples of two batches is similar, which signifies uniform burning of the binder.

The surface of the specimens exhibits irregularity, which is a result of the contact with support tissue inserted in the mold; this tissue helps in the prevention of surface erosion during the de-molding of the specimens. The range of dimensions for the individual edges of specimens has also been shown for the homogeneous group in Figure 4.17 and for the heterogeneous group in Figure 4.18. Although the repeatability of exact dimensions for each round of injection is not feasible, the range of dimensions for specimens has been shown to encompass all the extremes.

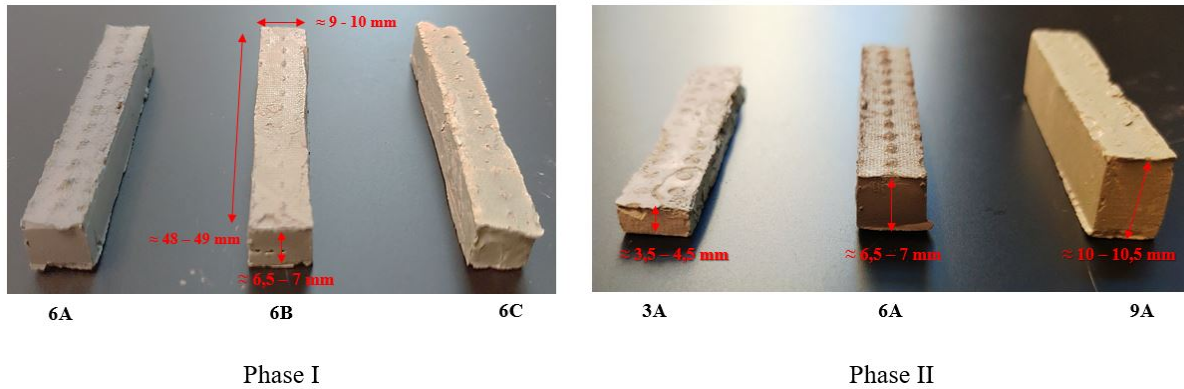


Figure 4.17 Specimens of phases I and II: the irregular surface is leveled by abrasion. These groups constitute the homogeneous formulation.

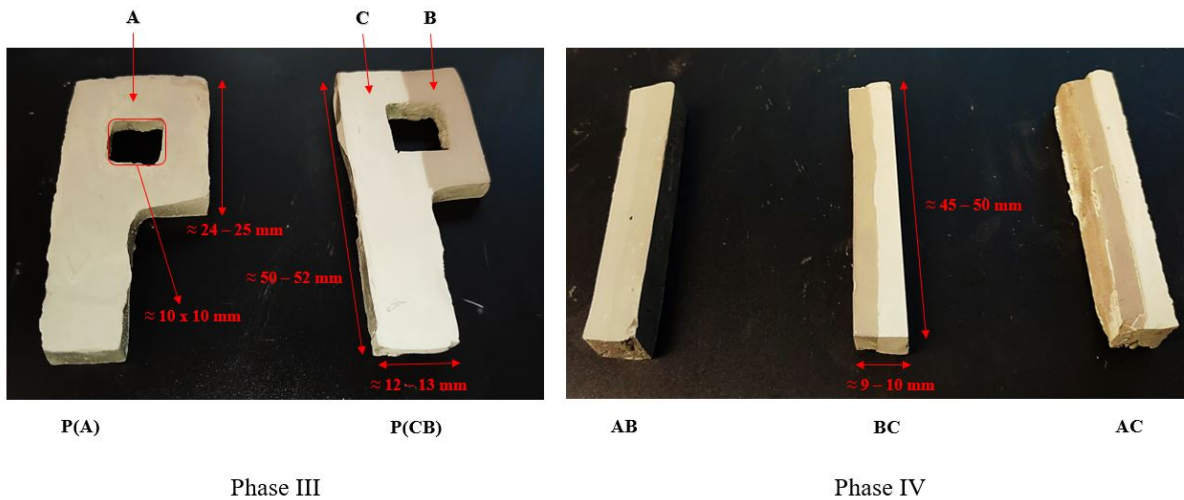


Figure 4.18 The heterogeneous group that constitutes phases III and IV, this group incorporates a modified injection strategy.

The geometrical measurement of the specimens is performed by identifying four points on the surface of all the rectangular sides. The mean takes into consideration the differences in

the surface topology and the inaccuracy that comes with it (Figure 4.17). For phases I and II, it is simpler to demonstrate the range of dimensions and the difference in the design. The different dimensions have been tabulated for phases I and II to provide a designation system for specimens based on morphological characteristics.

Consolidated SiC matrix is susceptible to chipping and erosion of the surface at smaller scales. The geometric dimensions of the specimens are recorded using a caliper. The precision of the caliper is determined to be ± 0.01 mm. The specimens are then subjected to capillary imbibition tests for the initiation of the poral network characterization. In the next sections, the characterization techniques will be discussed and justified for their use.

4.3 Characterization of poral network: capillary rise experiments

The characterization of poral network comprises all the experimental and simulation stages. Each phase is concerned with the quantification of relevant properties based on the constraints for the specimens in each phase. It becomes necessary to characterize porous matrices in order to understand their physical and chemical characteristics and maximize their performance. Characterization normally consists of many methods, beginning with the determination of bulk parameters such as porosity, pore size distribution, and pore morphology. The different experimental methods used to characterize the poral network of SiC granular specimens are summarized in Figure 4.19.

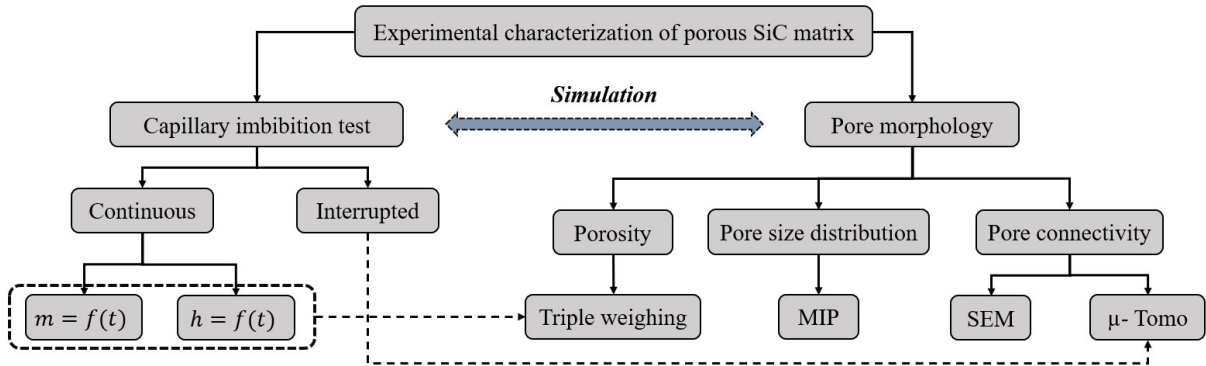


Figure 4.19 Schematic of experimental characterization of SiC matrix, the correlation between the imbibition kinetics and pore morphology is abridged with simulation.

In addition to regularly used techniques such as porosity measurement and electron microscopy, three-dimensional analysis utilizing tomography has grown in popularity for characterizing porous ceramic matrices. Tomography enables non-destructive three-dimensional characterization of macro pores and cracks that influence capillary flow. This approach is

particularly beneficial for the observation of capillary flow front that could be revealed in interrupted tests with fluids enabling X-ray intensity contrast. The major characterization steps incorporated for this research work are presented in the present Section 4.3 and the following Section 4.4.

4.3.1 Capillary imbibition test at room temperature

The quantitative determination of the effect of relevant parameters is included in the design of capillary rise experiments. The complete schematic is subdivided into continuous and interrupted tests. They both incorporate capillary imbibition in the SiC matrix, but the purpose of the two tests is different, as is the expected outcome. The major points of the capillary rise test and the classification have been presented in Figure 4.20.

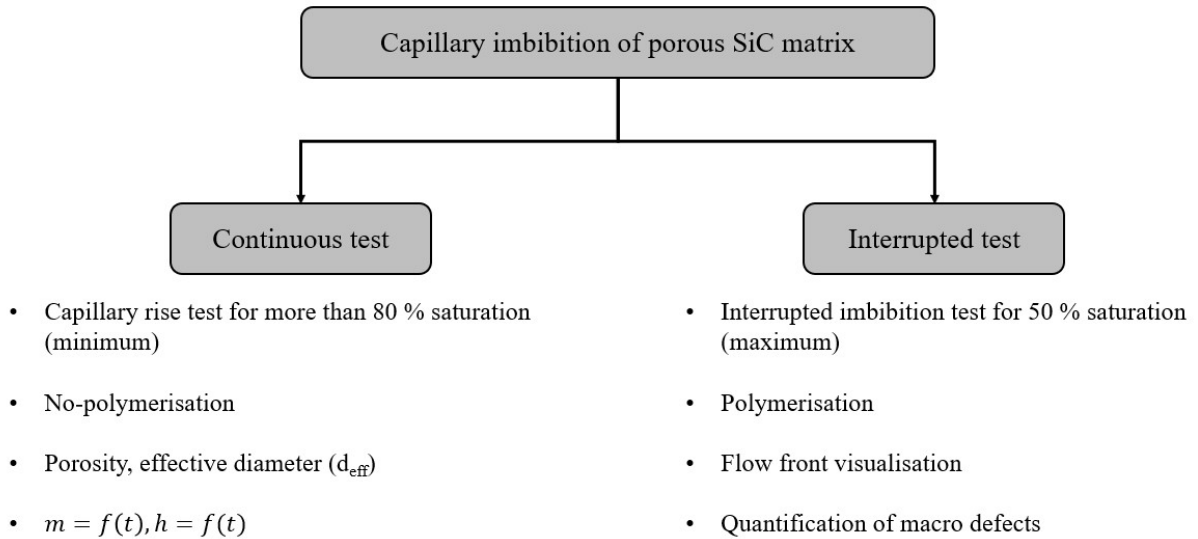


Figure 4.20 The classification of capillary rise experiments includes both continuous and interrupted approaches for the characterization of poral network and its visualization.

Experiments on continuous capillary rise are conducted at a saturation level exceeding 80%, which allows for a sufficient duration for complete development of capillary imbibition. The primary objective of the test involving *exo*-DCPD interruption pertains to the visualization of the flow front as it traverses through the matrix, with the aim of comprehending the flow hierarchy.

The significance of the polymerised flow front in defining capillary imbibition is influenced by the presence of defects and pores of varying scales. The concept of representing the porous network as a singular capillary tube, denoted by its effective diameter, is an idealization commonly employed in academic literature. The study employs two methodologies to examine

the uninterrupted ascent of mass and height in capillaries. The aim is to explore the production and impact of the saturation gradient that arises from the initial thermal processing of SiC granular consolidation.

The experiments of capillary rise in porous SiC specimens were carried out by using highly wetting fluids at room temperature. For continuous capillary rise tests, pure n-hexadecane (Acros Organics, 99 %) was used. The justification for the choice of model fluid for imbibition tests has already been given in detail in Section 3.1. The selection is based on the ratio of viscosity η to surface tension γ that should correspond to the range where capillary phenomena prevail.

Fluid	Formula	Description	Density	Flashpoint	Boiling point	Viscosity	Surface tension
n-hexadecane	C ₁₆ H ₃₄	colorless, odorless	0.7701 g/cm ³	135 °C	287 °C	3.474 mPa·s	27.47 mN/m

Table 4.4 General properties of n-hexadecane used for continuous capillary imbibition tests [144].

The model fluid that was utilized for the interrupted test is dicyclopentadiene (DCPD). In its *exo* form, it can polymerize quickly to stop the progression of capillary flow. Since the goal of using this model fluid for interrupted tests is to be able to observe the saturation of the flow front and the preferential path for fluid flow in the 3D poral network, it should be detectable under X-ray tomography. This is the reason for the addition of tin-based doping salt dibutyltin dilaurate (DBDTL) to the *exo*-DCPD resin at a concentration of 9 % vol. The procedure to elaborate the *exo*-DCPD resin is schematized in Figure 4.21. The detailed description for the preparation of *exo*-DCPD is beyond the scope of this thesis; therefore, a brief description of each step of the procedure is provided below.

1. This stage is associated with the separation of *endo* and *exo* from dicyclopentadiene (DCPD). For successful polymerization, the DCPD should contain only *exo*. DCPD is heated to 170 °C for 15 minutes and then at 190 °C for 4 - 6 hours.
2. The final distillation is done under vacuum at 60 °C for 2 - 4 hours. This step gives approximately 95 % of *exo*-DCPD.
3. The validation for the solution is done with RMN analysis for one hour in CDCl₃. The purity should be above 95 % for it to be used for interrupted tests.
4. The doping of the obtained *exo*-DCPD is necessary and it is achieved by adding a tin-based salt, dibutyltin dilaurate (DBDTL). For tomography visualization, 9 % vol. of this tin-based salt proved to be optimal for tomography visualization.
5. The catalyst is prepared while the interrupted test is ongoing to avoid any delay and

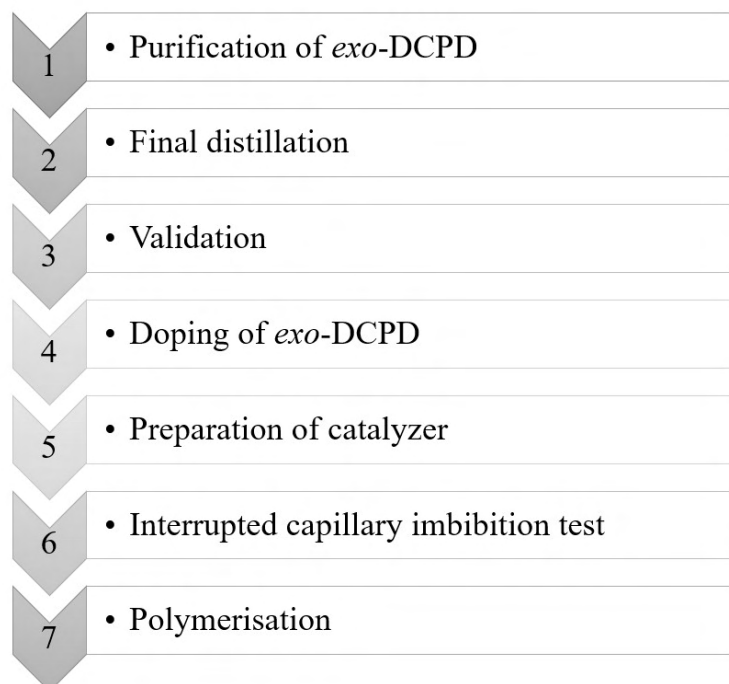


Figure 4.21 Procedure for the preparation and use of *exo*-DCPD for interrupted capillary imbibition tests for 3D visualization of flow behavior.

degradation of the catalyst if it is stored for too long a duration.

6. The doped *exo*-DCPD with 9 % vol. DBDTL is ready to be used for interrupted capillary rise tests.
7. When the desired level of capillary rise is attained, the specimen is separated from the bath containing the resin and put in contact with the catalyst that starts the quick polymerization.

The *exo*-DCPD was obtained from ChemSampco (Texas, USA), and the purification was completed at the MIL campus of the Université de Montréal (UdeM). Grubbs catalyst (Aldrich M1a Umicore 97 %) is used to polymerize *exo*-DCPD. It is combined with tricyclohexylphosphine (PCy₃) (Aldrich Chemistry) and toluene (PTI Process Chemicals) as a solvent. PCy₃ is a dangerous and annoying substance. Toluene is a toxic, poisonous, unpleasant, and flammable substance for human health. The sample is then put in a furnace at 70 – 80 °C for 48 hours to evaporate the non-polymerized *exo*-DCPD. The relevant properties of the doped *exo*-DCPD that were measured at Polytechnique Montréal are given in Table 4.5.

Fluid	Formula	Description	Density	Viscosity	Surface tension	Contact angle
<i>exo</i> -DCPD	C ₁₀ H ₁₂	Toxic if inhaled	0.985 g/cm ³	2.30 mPa·s	24.36 mN/m	0°

Table 4.5 General properties of *exo*-DCPD with tin-based doping agent which is used for interrupted capillary imbibition tests measured in-situ.

The selection of both model fluids was based on the similarity of their flow behavior compared to that of the silicon that is impregnated during melt infiltration at high temperatures. Since the scope of this research is limited to ambient temperature, neglecting the chemical reactions, emphasis has been given to fluids that present a ratio of viscosity to surface tension that is low enough to result in a capillary number $Ca < 10^{-6}$ corresponding to dominating capillary phenomena. The three fluids and their combined properties are presented in Table 4.6 to allow for the comparison of different parameters. Here we can observe that the properties of silicon are higher for surface tension and density. The model fluids have higher values for viscosity. The omission of effects of high temperature and the chemical reaction that occurs for silicon at high temperature during MI at 1450 °C is then justified for explaining capillary phenomena [22].

Fluid	Formula	Density (g/cm ³)	Viscosity (Pa·s)	Surface tension (mN/m)	Contact angle (°)
Silicon	Si	2.33	9.4×10^{-4}	860	40
n-hexadecane	C ₁₆ H ₃₄	0.770	3.0×10^{-3}	27.47	0
<i>exo</i> -DCPD	C ₁₀ H ₁₂	0.985	2.3×10^{-3}	24.36	0

Table 4.6 Comparison of the two model fluids with liquid silicon which is used for fabrication of MI-CMC components. The *exo*-DCPD here is doped with 9 % vol. DBDTL.

In both continuous and interrupted capillary rise tests, the model fluid is impregnated through the fabricated SiC specimens that replicate the SiC matrix in a composite. The capillary rise experiment setup (Figure 4.22) consists of an enclosed chamber that isolates the whole setup from outside surroundings. This is required because mass acquisition must be precise and error-free. Also, although n-hexadecane used for continuous tests poses a reduced health hazard, the situation is different for interrupted tests since *exo*-DCPD is harmful for health of people if not handled with caution. Therefore the test is performed under a closed and ventilated environment.

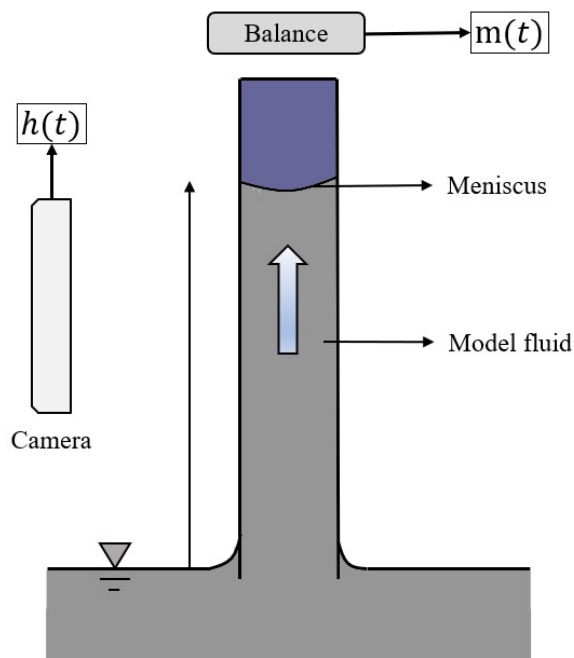


Figure 4.22 The two systems for the acquisition of mass and height of flow front for the capillary imbibition in porous SiC matrix.

The model fluid is stored in a clear bath. The bath is situated on a moving platform that is powered by a motor. The platform ascends until the model fluid and specimen surface make contact. There is a mass limit at which the arrangement becomes static. This allows for constant contact between the fluid surface and the specimen. This creates a pathway for the imbibition to begin.

The sample is allowed to hang below the mass balance so that the change in mass may be accurately recorded. In order to record both still photos and moving video of the impregnation procedure, a camera is used as shown in Figure 4.23. When the model fluid infiltrates the porous SiC specimen, the acquisition of mass and height begins at the same time. This assures that there is a possibility of an association between the increase in height and the related mass at particular time intervals. A LabView data acquisition system is used to collect mass data in order to evaluate the effective diameter characterizing the porous media.

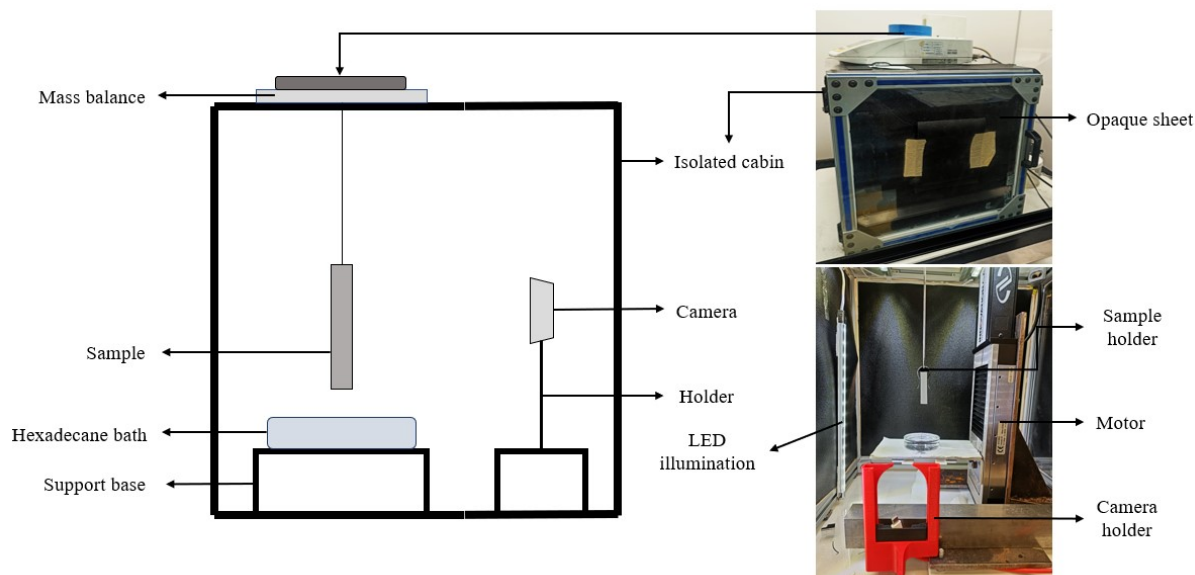


Figure 4.23 Experimental setup utilized to perform capillary rise experiments. The closed chamber reduces the possibility of error in the measure of mass, protects against toxic vapors and provides better contrast for the visualization of the surface flow front.

For the continuous tests, the impregnation is carried out for more than 80 % of the length of the specimen (100 % is preferred), since this would quantify the overall effect of the porous network. For the interrupted test, the impregnation is stopped once the capillary height has reached not more than 50 % of the length of the specimen. The impregnated model fluid is then subjected to catalysis, which polymerizes the *exo*-DCPD.

4.3.2 Tracking of mass

For the tracking of mass, the experimental setup is simpler. It consists of a hexadecane bath with a connecting probe to the mass balance. The mass measurement is extremely sensitive to changes in the surroundings; therefore, the complete setup is enclosed in a chamber. There is a provision made in the enclosed chamber to be able to see the initiation of capillary imbibition. A Sartorius CP323 analytical lab balance scale is used to record the weight of samples. The lab balance has a precision of ± 0.01 g. This balance is attached to the capillary test setup. The enlarged image for the continuous capillary rise test can be seen in Figure 4.24.

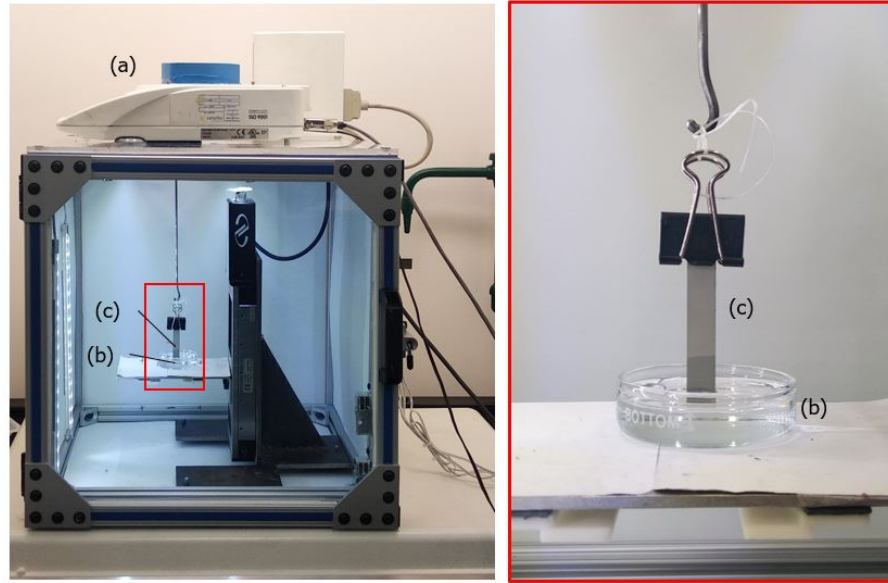


Figure 4.24 Continuous capillary imbibition setup with the enlarged perspective for the specimen (c) and the model fluid (b). The specimen is attached to the lab balance (a) with a probe that has to be stationary for accurate recording of mass increment [140].

As soon as the rectangular bottom cross-section of the specimen touches the model fluid, capillary absorption begins. The contact surface of the sample should be parallel to the surface of hexadecane. There is a sudden rise in the fluid, which forms a meniscus. The sudden formation of the meniscus has to be corrected so as to remove the initial capillary jump in the mass recording. As the imbibition progresses, the flow rate is normalized and decelerated since the length of the effective capillary column is reduced with the impregnation of the poral network with hexadecane. A LabView interface (Figure 4.25) is developed for recording the capillary imbibition and visualizing the imbibition curve for each test.

A brief description of the different panels and tools in the LabView program is given below:

1. This panel controls the direction and absolute speed of the platform that supported the hexadecane bath.
2. This bar shows the absolute speed of the fluid bath. The speed can be modified as per requirements.
3. This panel controls the vertical motion of the fluid bath based on two progression modes.
4. This initiates the recording of the imbibition data.
5. The specimen dry mass and laboratory conditions are recorded for each imbibition test.

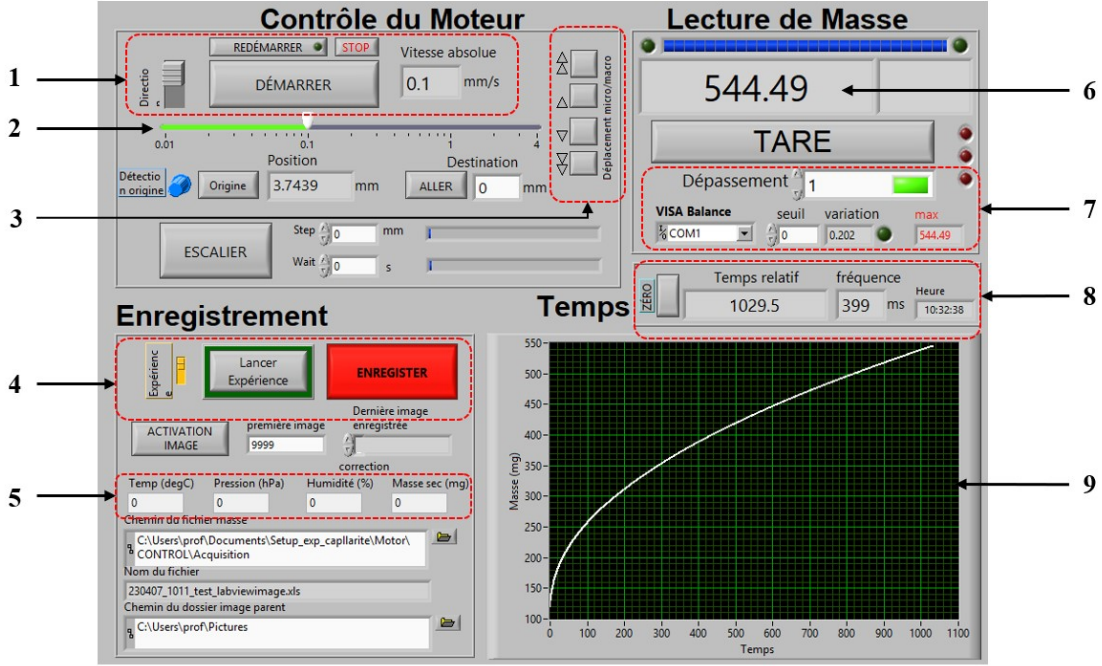


Figure 4.25 The LabView interface that was developed for the recording of mass for capillary imbibition tests.

6. This shows the real-time mass for the test; this is not a constant value and gradually increases.
7. This is the communication interface between the modules of the capillary setup.
8. This panel gives information about time management and data acquisition frequency.
9. The real-time imbibition curve is presented in this space.

The capillary rise experiments use the Washburn approach to describe capillary imbibition, where an overall poral network is considered as a single capillary tube of diameter d_{eff} ($d_{eff} = D_{cap} = 2R_{cap}$). The single capillary tube model would not be an ideal consideration, but it would include all the effects of the different forces that combine for imbibition to occur. The parameters that are used for the calculation of the effective diameter are given the following equation resulting from the Lucas-Washburn law:

$$d_{eff} = \frac{m^2}{t} \frac{4 \eta}{\rho^2 S^2 \varepsilon^2 \gamma \cos \theta} \quad (4.1)$$

where m is the mass of impregnated fluid, S is the cross-section of the specimen, ρ is the density of the fluid and ε is the porosity of the specimen determined by one of three methods

(geometrical, buoyancy and Hg porosimetry) that will be described in Section 4.4.1. The mass-tracking approach is considered to present similar results for porosity as compared to the height-tracking approach. However, it necessitates two additional parameters that include the cross-sectional surface and the theoretical porosity to evaluate the effective diameter d_{eff} . This effective diameter is then determined by the analysis of the imbibed mass $m = f(t)$ from the slope (m^2/t) of the curve which is a straight line for Washburn imbibition.

4.3.3 Tracking of height

This way of keeping track of the height of the moving flow front is different from mass tracking in that it has different requirements. The primary source of image acquisition was the GoPro-8, with a secondary substitute of a mobile phone camera. For phases III and IV, the camera setup was modified for better resolution and ease of post-processing of images and videos. An example of image processing giving segmented view of the position of the fluid flow front is shown in Figure 4.26.

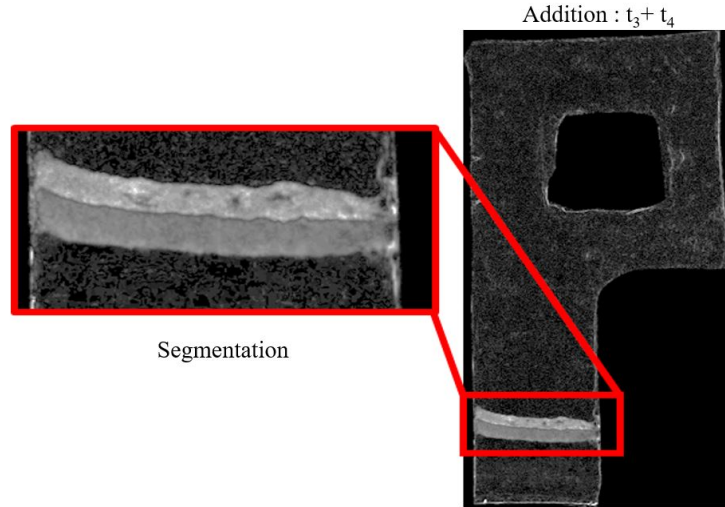


Figure 4.26 Segmented view of the area of interest to determine the infiltrated mass with the image analysis for a P shape specimen with central cavity.

Here, the primary objective is to acquire accurate visuals of the flow front so as to mitigate any erroneous conclusions. Therefore, the camera setup has been upgraded as per the post-processing requirements. A visual processing protocol is used to figure out the effective diameter, which is the same as the capillary diameter when height is being tracked. A Matlab script has been developed that calculates the effective diameter using the Washburn equation that is given by:

$$d_{eff} = \frac{h^2}{t} \frac{4 \eta}{\gamma \cos \theta} \quad (4.2)$$

The tracking of height employs the camera to take images at 60 seconds intervals, and then successive effective diameters are computed for the height, and then the ultimate diameter is acquired. A Python script described elsewhere [145] has been used to turn the flow front into an effective diameter. This approach also assists in the validation of the numerical simulation for capillary imbibition. The Equation 4.2 to determine the actual effective diameter is not affected by the porosity or cross-section of the specimen. This prevents errors that could occur when measuring the sample size.

With this, the volume of infiltrated hexadecane is calculated by incorporating the porosity that represents the majority of the open porosity of the SiC matrix. The equation to calculate the volume of hexadecane is given by:

$$V_{hexa} = A * \varepsilon * w_{avg} \quad (4.3)$$

where V_{hexa} is the volume of hexadecane infiltrated, ε is the porosity and w_{avg} is the average thickness for the segmented sectional image. The developed python script permits to obtain the fluid progression as height based on time ($h = f(t)$) and calculating the actual effective diameter using the slope of the graph ($h^2 = f(t)$). The acquisition is done in both image and video formats. The images are recorded every minute, while the video is recorded during the entire duration of imbibition.

A discrepancy in predicted mass resulted from the two procedures; the mass approach is more precise as it contains the whole infiltrating mass of hexadecane. For the computed mass from height tracking, there is an underestimation of the mass (Figure 4.27) that suggests the potential of a difference in saturation that translates to a saturation gradient between the surface and core zone of the SiC matrix.

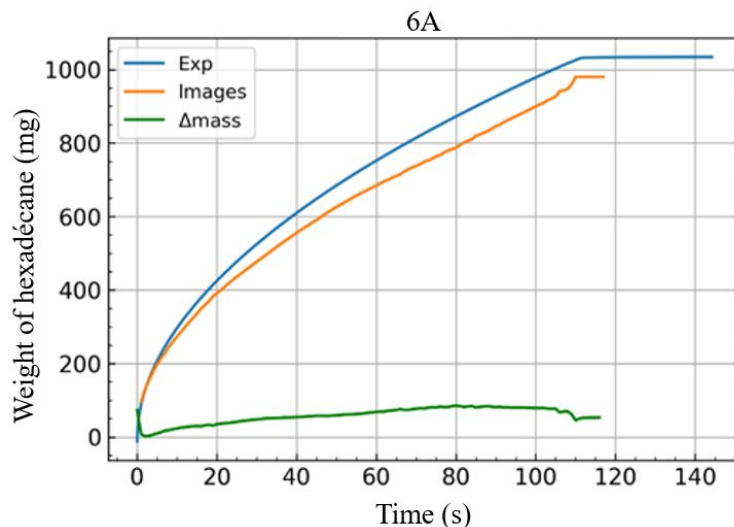


Figure 4.27 Typical curve for 6A specimen that exhibits distinct difference in mass measured by mass tracking (Exp) from that computed through height tracking (Images).

4.3.4 Interrupted test with *exo*-DCPD

Once the doped *exo*-DCPD is prepared, the interrupted capillary stage can begin. The capillary rise is performed until the flow front reaches 50 % of the total specimen height. The specimen is then extracted from the confined test apparatus and moved to a fume chamber. This step is required to prevent health complications resulting from contact with toxic compounds. The tin-salt-based catalyst is distributed over a glass dish, and the cross-section of the specimen is put in contact with it. The surface contact initiates polymerization, and the specimen is positioned for 15 to 20 minutes to complete polymerization. The specimen is then transferred to a ventilated oven for complete drying, which mitigates the *exo*-DCPD toxic vapor.

The specimens are dried for 48 hours to completely remove the traces of a pungent smell that is toxic if inhaled directly. This interrupted test approach allows for a three-dimensional visualization of the porous network that includes all the defects at different scales. For interrupted tests of complex geometry, both homogeneous and heterogeneous specimens would provide the effect of changing the effective wetting section.

The cumulative duration of an interrupted test is significantly lengthier than that of the hexadecane test. For every round of polymerization, a new catalyst must be prepared. The interrupted capillary tests would provide a quantitative method for understanding the influence of two interconnected poral groups on heterogeneous specimens.

In order to comprehend inter-layer capillary imbibition, the role of the interface is crucial. As proposed by the mass tracking approach for poral network characterization, each formulation in a heterogeneous formulation would be equivalent to a single capillary tube having each their own effective diameter.

4.4 Characterization of poral network: porosity and size distribution

Pore morphology is an important metric that describes porous materials. It includes pore size distribution, spatial pore connectivity, and pore shape. Characterization techniques such as X-ray tomography and scanning electron microscopy (SEM) can be used to observe the internal structure of a porous material and assess the spatial connectivity of the pores. Pore shape is important for understanding the characteristics and performance of porous materials, as it helps to develop and improve porous materials for a variety of applications.

4.4.1 Characterization of porosity

In this project, the porosity is being characterized based on different methodologies that correspond to distinct calculation approaches and omission of certain parameters. The geometrical, buoyant, and mercury intrusion methodologies are used to ascertain the initial degree of porosity in all specimens as shown in Figure 4.28. This provides with a greater effect of incorporating various methods and based on the results, a comprehensive explanation can be given for the precision of porosity measurement for each method.

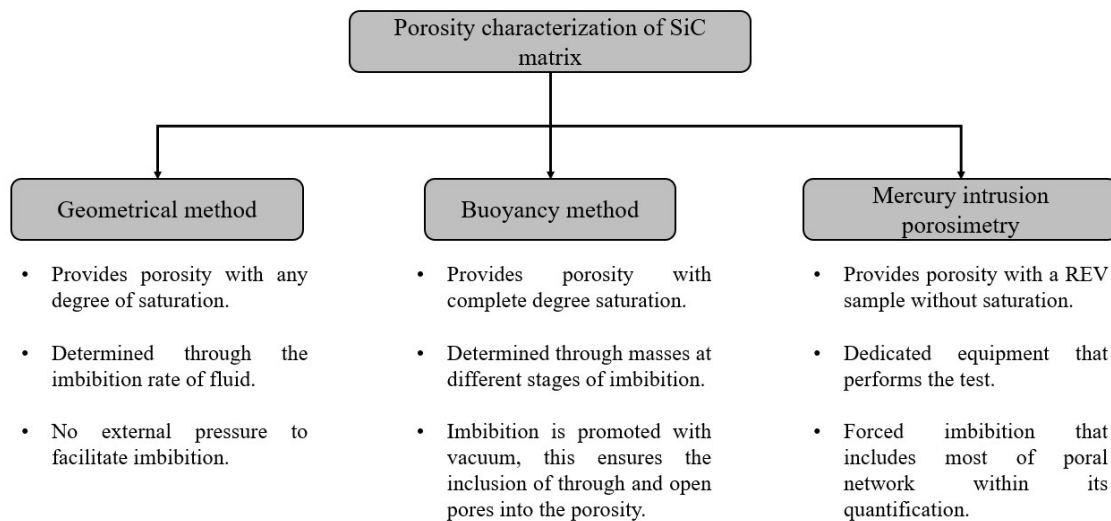


Figure 4.28 The figure presents some porosity characterization methodologies and brief notes to provide an overview of the processes. The accuracy of the method increases from geometrical to mercury intrusion porosimetry.

Porosity: geometrical method

The total geometric porosity ε_{Geo} of the specimen is calculated from its dimensions. It is estimated based on the Equation 4.4 derived from the ratio between the full density of the SiC (3.21 g/cm³) and the apparent density of the specimen given by equation 4.5. The geometric porosity is determined for each specimen per phase as part of the characterization of the poral network with growing precision.

$$\varepsilon_{Geo} = 1 - \frac{\rho_{specimen}}{\rho_{SiC}} \quad (4.4)$$

$$\rho_{specimen} = \frac{Mass_{specimen}}{Volume_{specimen}} \quad (4.5)$$

To determine $\rho_{specimen}$, it is necessary to weigh the porous specimens and measure their linear dimensions. It is thought that the density of the SiC is an absolute value and therefore it possesses no uncertainty of measurement. The apparent volume of the specimen is derived from its dimensions defined as l for length, w for width, and e for thickness. The dimensions of the specimens are measured with a caliper with a precision of ± 0.01 mm. The average dimensions of four measurements is determined and the uncertainty on the measurement of the volume is 0.29 %.

Each specimen is weighed once. The measurement uncertainty on the mass of the specimens is 0.02 %, based on the absolute inaccuracy of measuring the mass which is ± 0.01 g. The uncertainty in estimating the geometric porosity is thus 0.31 %.

This method has the advantage of evaluating the porosity of the whole specimen. In addition, the evaluation of porosity takes into account the open and closed pores. However, the main disadvantage of the method is related to the low precision in the evaluation of the parallelepiped volume of the specimens that are not sharply defined.

Porosity: triple weighing (buoyancy method)

Over the course of the study, curiosity about the porosity measured by triple weighing began to emerge. We took advantage of capillary imbibition tests to completely fill the open porosity of specimens with hexadecane. With this approach, the resulting porosity is more in line with that of the real poral network, which has a noticeable effect on imbibition kinetics.

Errors related to the measurement of the dimensions of irregular shape specimens cause geometric porosity measurement to overestimate their true porosity. The relative error in volume measurement may be too high to be considered acceptable. The triple-weighing

method eliminates the need to measure the volume of the specimens.

This method is based on the measurement of three masses and follows the ISO 5017:2013 standard. The first called m_1 is the dry mass of the specimen. The second mass m_2 is the mass in the air of the specimen when it is impregnated with hexadecane. To obtain this impregnation, three-quarters of the specimen is immersed in a hexadecane bath. The specimen is not submerged completely so that the air present in the pores can be evacuated to ensure that there is no trapped air in the specimen and that hexadecane impregnated completely the open porosity of the porous network. The immersed specimen is placed under a vacuum bell for 24 hours. After this time of impregnation, the specimen is removed from the hexadecane bath and weighed; the resulting mass is the moist mass m_2 .

The third mass m_3 is measured when the hexadecane-impregnated specimen is immersed in hexadecane. The Archimede's push then results in an immersed mass lower than the moist mass measured in air. Equation 4.6 is used to calculate the total porosity ε_{Twe} of the specimens.

$$\varepsilon_{Twe} = \frac{m_2 - m_1}{m_2 - m_3} \quad (4.6)$$

As a consequence of using this method, the value of ε_{Twe} corresponds to that of open porosity only. However, since the level of granular porosity in the samples is quite high, in the order of 40 %, it is reasonable to believe that the amount of closed porosity is negligible. The masses were measured with a scale allowing a precision of 0.1 mg. The uncertainty of the calculation of the porosity obtained by triple-weighing is 0.01 % and is related to the uncertainties in the measurements of the masses only.

It can be observed that the triple-weighing method measures a porosity closer to the actual porosity of the specimen, and it also allows to have a lower measurement uncertainty than that obtained when calculating the geometric porosity. Considering the precision of this method for evaluating the porosity and the fact that it is applicable to the whole volume of the specimens, this method was taken as the basis for the determination of specimen porosity.

Porosity and pore size distribution: mercury intrusion porosimetry

Mercury intrusion porosimetry (MIP) is a popular technique for determining the pore structure of porous materials such as ceramics. MIP works on the premise that mercury does not wet the surface of most materials. This means that mercury can only enter the pores of the material at a specific pressure, which is inversely proportional to the size of the pores. The Laplace's pore diameter corresponding to a given intrusion pressure is based on the model

of a straight capillary tube. The quantity of mercury intruded is measured at each pressure, and this information is utilized to compute the pore size distribution and total pore volume.

The MIP was completed at the MIL campus of the Université de Montréal at the Montreal Area Platform for Electrochemical Systems (MAPLES). MicroActive Autopore V 9600 was used to conduct the MIP experiments. Due to the geometrical restriction imposed by the apparatus, the samples were extracted from the larger specimens, and their size was reduced to acceptable limits ($10 \text{ mm} \times 4 \text{ mm} \times 4 \text{ mm}$). This restriction on using the actual-sized sample evokes the necessity to correlate the overall poral network to a reduced representative volume.

In order to illustrate a distribution of effective pore size, it may be expressed as the differential incursion volume that can be associated with Laplace's pore diameter as shown in Figure 4.29.

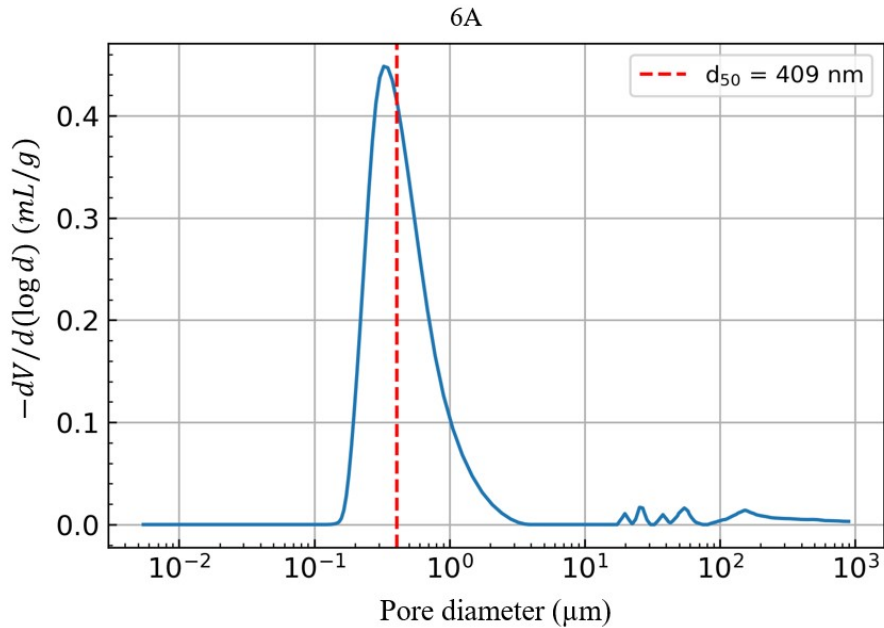


Figure 4.29 Typical MIP curve that presents the spatial distribution of pore diameter, with the evaluation of the median pore size d_{50} . The range of pore diameters is crucial in the quantification of poral network.

The area of the regions that lie below the peak of this particular kind of curve is crucial due to the fact that they are equivalent to the pore volumes of each Laplace's pore size fraction [146]. These curves also make it easier to see the areas of the intrusion curve that have a greater steepness of the intrusion pressure gradient.

From the cumulative pore size distribution representation, it is possible to evaluate the d_{50} value corresponding to the median diameter of pores, below which 50 % of the pores are

smaller. This quantity is important in the modeling of the microstructure of porous materials. The use of the median pore-throat radius is a significant parameter to estimate the permeability suggesting that d_{50} may govern fluid flow in porous media [147]. Nonetheless, it is important to recognize that mercury porosimetry has limits. One of the most significant disadvantages is that it only measures the size of the entry into a macro pore, not the true interior size of the hole. It also cannot be used to evaluate closed pores for obvious reasons, since the mercury has no method of entering that pore. The pore network (cross-linking structure between pores) may be interpreted using several software tools. However, it is important to note that several assumptions are made during the process, and the final conclusions are rather arbitrary [148].

In terms of accurate representation of the poral network as a representative volume, the porosity obtained by MIP is the most accurate for measuring open porosity. However, the main disadvantage of the method is related to the very small samples that could not be totally representative of the whole specimen. The MIP method gives them a local evaluation of open porosity. This method will be used to characterize locally the porosity of heterogeneous specimens.

4.4.2 Spatial pore connectivity: scanning electron microscopy

Scanning electron microscopy (SEM) magnifies images of a specimen to reveal different features of its microstructure (defects, grain size, pores, chemical composition, crystal structure). SEM aids significantly in the domains of material sciences and surface sciences. It is a significant tool in the magnification of internal structures several times to see and analyze the surface structures [149–151].

The samples of SiC porous material (after heat treatment) have to be prepared for SEM observation, which is a protocol to be followed in itself. The preparation of samples begins with the cutting of larger specimens into smaller parts with a diamond saw. The samples are then dried to eradicate any residues of moisture. The samples are mounted in epoxy resin and require 15 hours for complete curing of the epoxy. After mounting, the samples are subjected to a series of polishing phases for obtaining the optimum degree of detail in the microstructure that would qualify the samples for SEM observations. The different polishing phases are enumerated in Table 4.7.

The grinding with 600-grit foil is for flattening the surface, followed by 240-grit fine grinding. After each polishing step, the sample has to be cleaned well with soap and checked under a microscope before moving on to the next polishing step. The microscopic verification for this grinding stage is to have unidirectional grinding lines on microscopic observation.

Sequence	Grit size	Abrasive type	Turning speed (rpm)	Suspension	Duration (min)	Operation type
1	600	SiC foil	300	Water	7 - 10	Surface grinding
2	240	SiC foil	300	Water	7 - 10	
3	–	MD-Largo	150	Polycrystalline diamond (9 μm)	10 - 15	Mechanical polishing
4	–	MD-Largo	150	Polycrystalline diamond (3 μm)	10 - 15	
5	–	MD-Largo	150	Polycrystalline diamond (1 μm)	10 - 15	
6	–	MD-Chem	150	Colloidal silica + Hydrogen peroxide	15 - 20	Chemical/mechanical

Table 4.7 The polishing steps for the preparation of SEM samples. The process begins with micro-surface grinding. The final steps provide optimum quality of fine polishing for the characterization of the poral network of the SiC matrix.

The SiC foils were obtained from Struers manufacturer. For the mechanical polishing stage, MD-largo discs were utilized, which were also procured from Struers along with the polycrystalline diamond suspension. For mechanical polishing with polycrystalline suspension, the sample is rotated in the opposite direction as the disc.

After each polishing step, the sample has to be observed under a microscope to verify the quality of polishing, if at any step the quality of polishing is not optimal, the complete sequence has to be repeated. Mechanical polishing of SiC samples poses certain difficulties, such as the continuous erosion of SiC particles with every successive polishing step. This results in the presence of abrupt voids and matrix crack propagation due to the continuous polishing forces applied. The polishing protocol for SiC matrix was developed in situ at Laboratoire de Préparation et d'Observation des Matériaux (LaPOM) at Polytechnique Montréal. The successful completion of this polishing stage is followed by SEM observation.

The primary objective of this observation is to visualize the poral network in two dimensions and also enhance the difference between the different microstructures of the SiC matrix. This would enable both qualitative and quantitative analysis of the matrix. The flow dynamics can then be explained based on the morphological variations observed in the matrix microstructure.

The electron microscope utilized is the SEM-FEG JEOL JSM-7600F situated at the Centre de Caractérisation Microscopique des Matériaux (CM)² at Polytechnique Montréal. At SEM, the actual observation of the microstructure is based on parameters that have already been set for acquisition. Usually, for each SEM round, the maximum number of high-quality images are finalized, which are deemed best for post-processing. The images are acquired at $\times 3000$ and $\times 5000$ magnification with four to five sets of images per zone of interest. A good example of fine characteristics that could be observed on SEM is shown in Figure 4.30 where the interface between two formulations of slurry in bi-laminar specimens of phase IV is clearly seen.

Electron microscopy offers a crucial visualization of the poral network that forms the intricate

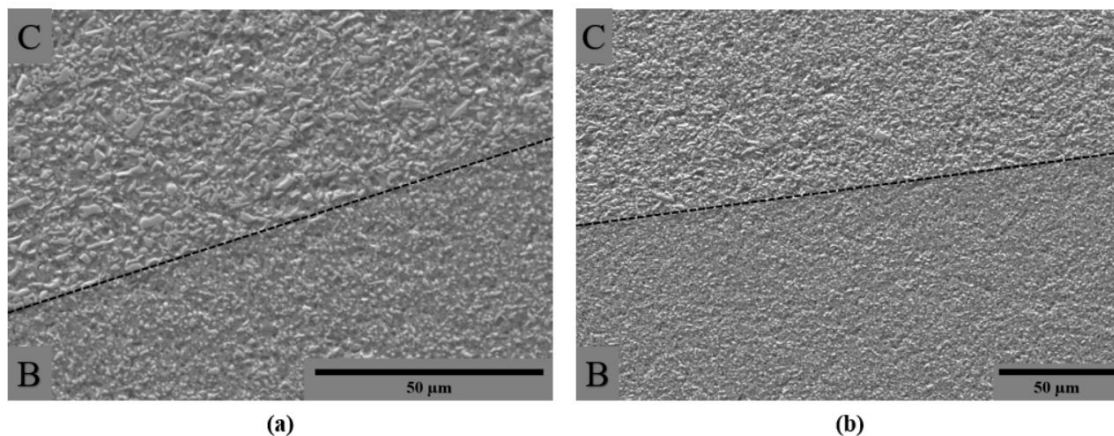


Figure 4.30 Comparison of the microstructure of two different slurry formulations identified by B and C for different magnifications: (a) is at $\times 1000$ magnification, while (b) is at $\times 500$ magnification to show the interface of the two microstructures in the same specimen.

pathways for the transmission of fluid. The visualization of hydraulic conductivity with a morphological view of the spatial spread of pores and other defects in the matrix. The MEB observation also offers a necessary source for the comparison of the microstructures for the three formulations (phase I) and for different thicknesses (phase II).

4.4.3 Spatial pore connectivity: X-ray tomography

Composites feature sophisticated three-dimensional, spatially dispersed structures that contain varying proportions of cracks and porosity. The pore morphology and connectivity refer to the intricate shape of the paths linking the pores inside a substance [152]. The spatial connection of the pores is critical because it impacts fluid and gas movement through the material.

To observe the internal structure of a porous material and assess the spatial connectivity of the pores, advanced imaging methods such as X-ray tomography can be employed. Conventional two-dimensional imaging techniques such as optical and scanning electron microscopy (SEM) can provide limited information on the 3D microstructure. Porosity characterization methods such as triple-weighing (Archimedes effect) and mercury intrusion porosimetry (MIP) cannot detect the closed pore structure [152].

X-ray computed tomography (XCT) is a relatively recent non-destructive approach for the 3D microstructure study of bulk materials, employing synchrotron or laboratory X-ray scanners. Compared with standard 2D characterization methods, XCT can give precise and high-resolution 3D analyses of the microstructure. The XCT method is exploited to observe the progression of capillary fluid front in interrupted tests. The tin-salt doped *exo*-DCPD permits

to reveal of the position of the interface between liquid and gas. The specimen from all four phases were analyzed with this characterization method.

The equipment used for the present study is the Xradia 520 Versa, developed by Zeiss and located at the Groupe de Calcul et de Modélisation (GCM) laboratory at Polytechnique. Considering the size of the specimens that were analyzed, a voxel resolution in the order of $70\text{ }\mu\text{m}$ was obtained. This resolution was not strong enough to observe micro pores associated with the granular SiC matrix, but sufficient to resolve macro pores and cracks.

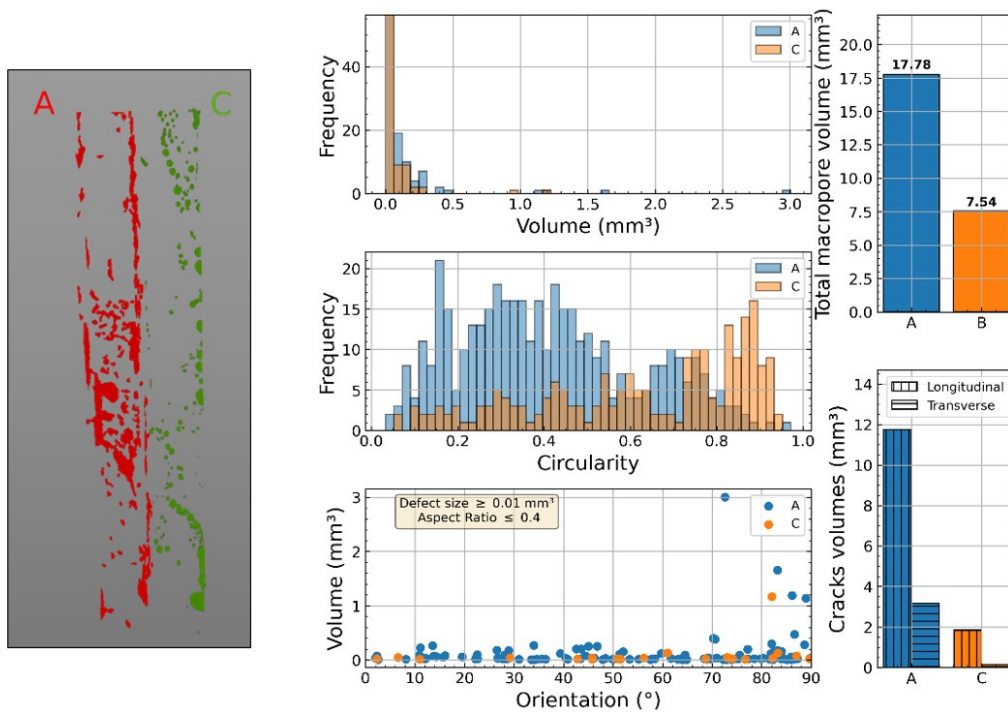


Figure 4.31 A representative characterization of a heterogeneous rectangular bi-laminar (AC) specimen with polymerised *exo*-DCPD. The nature and distribution of matrix defects provide detailed morphological analysis and its influence on the capillary phenomena. The equipment has a spatial resolution of $0.7\text{ }\mu\text{m}$ and a minimal achievable voxel of 70 nm .

A general representation of the defects characterization with tomography and Dragonfly software has been given to better understand the influence of matrix defects on the morphology and evolution of the progressing flow front as part of imbibition phenomena. The tomography provides significant information on the nature of macro defects and their volumetric quantification. An example of experimental results that can be extracted from XCT analysis is shown in Figure 4.31 where pores and cracks in a phase IV bi-laminar AC specimen are quantitatively analyzed.

The presence of micro-defects would alter the imbibition kinetics such that some regions

might experience different modes of pore filling by the model fluid. The circularity provides a quantification of the nature of the pore. When the circularity is closer to unity, the conventional pores have a completely circular boundary, while at lower circularity, the shape becomes more distorted. However, this stage will be detrimental to the characterization of the flow interface that interrupted capillary imbibition (SO2) generates. The presence of macro defects could induce a flow hierarchy between voids and matrix. The hierarchical sequence of capillary rise (SO4) would provide a better comprehension of underlying interactive forces acting at micro and macro scales to effectively complete the imbibition.

4.5 Simulation of imbibition: approach and experimental correlation

The experimental analysis of the pore network facilitates the development of a theoretical framework that incorporates material and fluid parameters to forecast infiltration kinetics and elucidate filling mechanisms.

The numerical simulation of capillary infiltration can be based on a model utilizing the Richards equation, as explained in Section 2.7.2. Solving of Richards' equation was obtained through the utilization of FlexPDE, a software package specifically designed for solving partial differential equations.

Apart from the pressure and saturation variables that form the basis of Richards equation, the main parameters, hydraulic conductivity and capacity, are based mainly on porous material characteristics and wetting fluid properties. The parameters that are related to the porous specimens will be given in Chapter 5 for specific specimens of each phase. The properties of wetting fluids (n-hexadecane and *exo*-DCPD) necessary to provide as inputs for the calculations were given in Table 4.6. For n-hexadecane, the values comes from [153] while for *exo*-DCPD, they were measured in laboratory at Polytechnique.

Other important parameters to provide for calculations are those related to the Van Genuchten relation (Equation 2.26) that couples pressure and saturation variables. In this equation, the parameter n characterizes the slope of the transition of saturation. The parameter α (in Pa^{-1}) gives the position in terms of pressure of the transition. The methodology to determine these parameters from mercury intrusion porosimetry (MIP) and their values will be given in Chapter 5 for each specific specimen.

The geometric description of rectangular specimens is established through the interconnection of four surfaces, and distinct boundary conditions are applied in accordance with varying scenarios. As shown in Figure 4.32 for typical rectangular specimens of phase I, a boundary condition of *no flow* is imposed to the two vertical surfaces and the top surface of the specimen. This means that the fluid cannot pass through these free surfaces. The capillary

flow is introduced in the specimen through the bottom surface where the negative capillary pressure is imposed as a boundary condition. This lead to a bottom-up capillary flow. In the case where specimens consist in heterogeneous poral network, as it is the case for example in bi-laminar specimens of phase IV (Figure 4.32), it is necessary to define boundary conditions at the interface of the two porous media to permit liquid flow through the interface, from one formulation to the other.

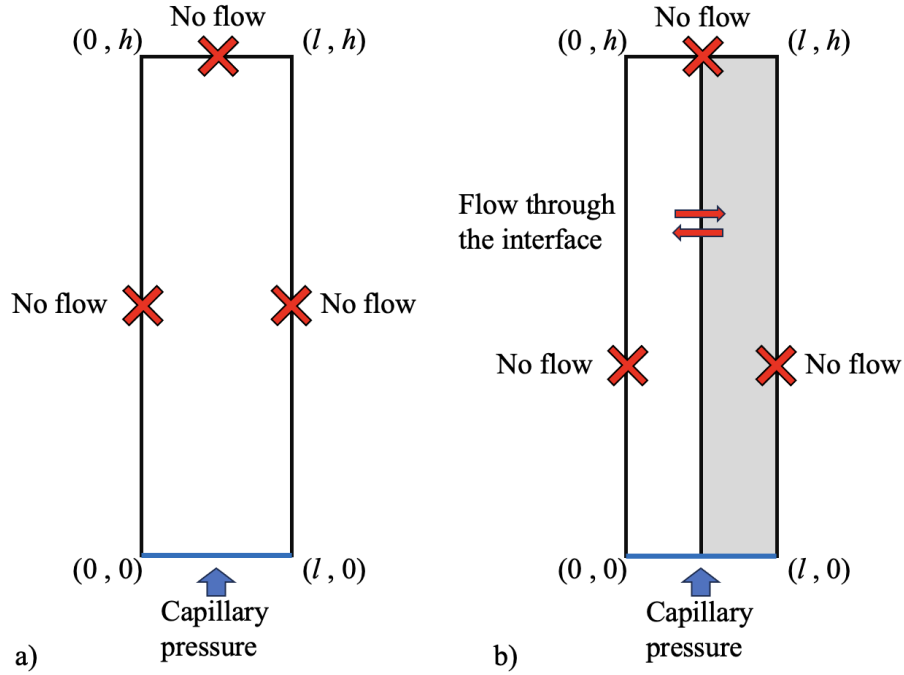


Figure 4.32 Definition of rectangular geometry of the specimens (h : height, l : width) and initialisation of the boundary conditions at the free surfaces, the interface between each porous material formulation for heterogeneous specimens and entry surface (bottom) for capillary fluid. a) Rectangular specimens of phase I; b) rectangular bi-laminar heterogeneous specimens of phase IV.

A mesh has been automatically generated to give more refined mesh size around the advancing flow front boundary, as depicted in Figure 4.33. As an output of the simulation, FlexPDE gives the pressure gradient and the saturation profile along the specimen. This is also shown in Figure 4.33. It is also possible to have as outputs the evolution with time of different variables for different positions in the specimen. As an example, Figure 4.34 shows the evolution of saturation at the bottom, middle and top of the specimen with time.

The model constructed utilizing FlexPDE software was composed with pressure as the primary variable. However, it also furnishes the saturation values of the medium, which ne-

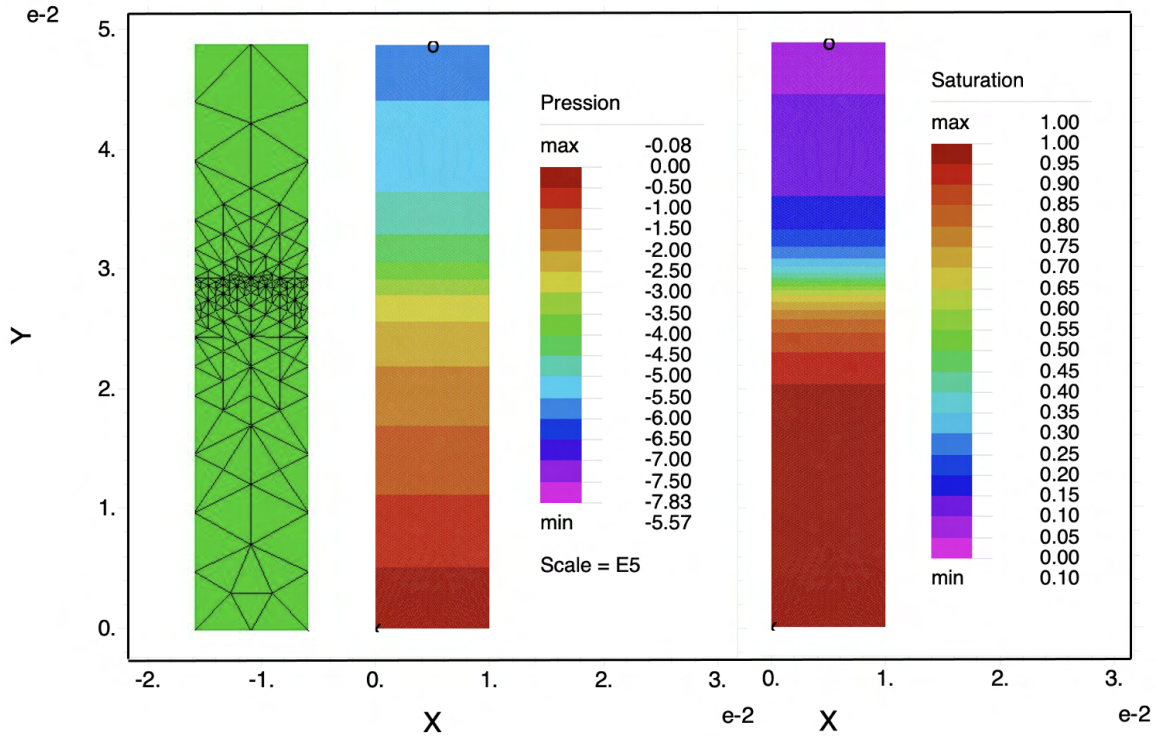


Figure 4.33 Generation of adaptive mesh (left) that shows refinement of the mesh size at the flow front. The corresponding capillary pressure gradient (center) and the saturation profile (right) are obtained for the same simulation time of 3000 seconds.

cessitates conversion into liquid mass via pore volume. This facilitates the comparison with Washburn's experiments, which furnish the $m(t)$ plot. It is possible then to obtain as output the curve $m^2(t)$ and compare it to the experimental one to *adjust* the tortuosity (input parameter) in order to obtain a good fit. A typical linear $m^2(t)$ curve obtained from simulation is shown in Figure 4.35.

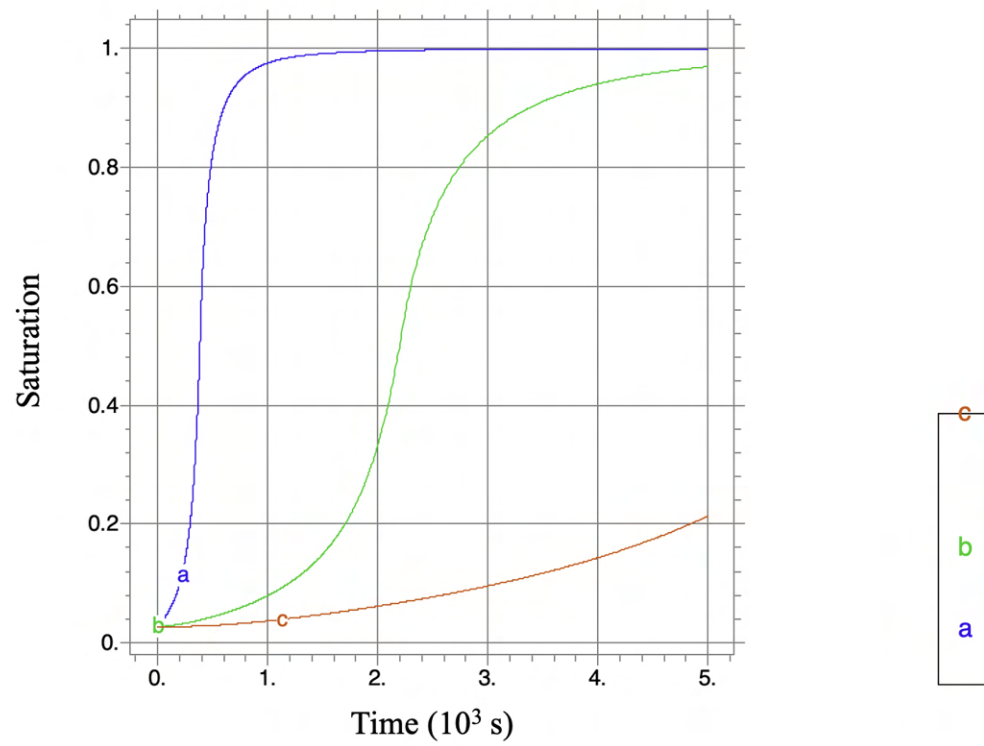


Figure 4.34 Prediction of saturation as a function of time for different identified zones in the specimen geometry.

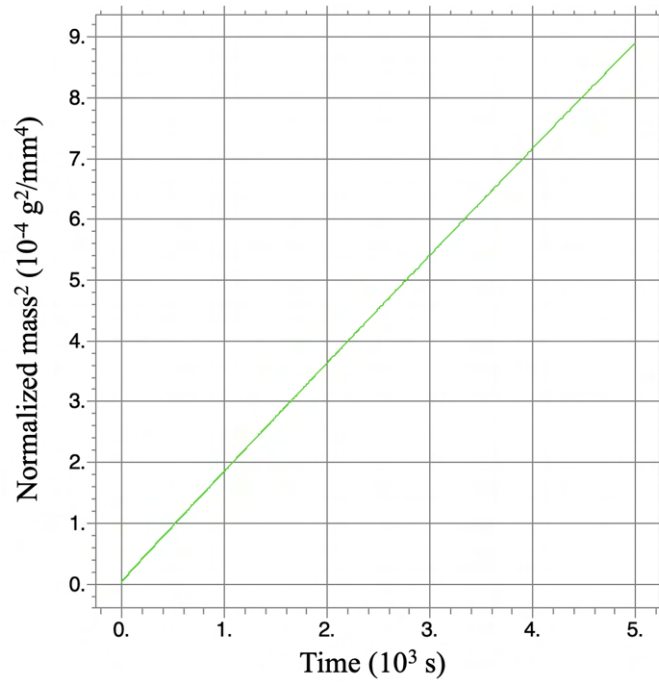


Figure 4.35 Square of the impregnated mass (normalized) as a function of time obtained from simulation.

As a summary, Table 4.8 gives most of the input and output parameters of the FlexPDE application that is used for solving the Richards equation.

Input	Technique	Comments
Dimensions	Geometrical measurement	Provide the geometrical spatial limits of the specimen.
Porosity ε	Triple weighing or MIP	Total open porosity of the specimens or of each formulation in heterogeneous specimens
Median pore size d_{50}	Mercury intrusion	Pore size of the specimen or of each formulation in heterogeneous specimen
Tortuosity τ	Imbibition curve fit	Effect of interconnected open pores in the matrix
VG parameters n and α	Mercury intrusion	Empirical shape that is related to pore size distribution [154]
Density ρ	Standardised value or measured	Obtained for standard temperature pressure conditions
Viscosity η	Standardized value or measured	Obtained for standard temperature pressure conditions
Output		
Saturation s	—	Obtained in response to the negative capillary pressure
Effective pore size d_{eff}	Numerical calculation from $m = f(t)$	Validation of the imbibition dynamics between exp. and simulation

Table 4.8 Input and output parameters for the numerical simulation of capillary flow in porous specimens.

CHAPTER 5 RESULTS AND ANALYSIS

This chapter provide the necessary progression of studies that improve the comprehension of imbibition dynamics of a SiC matrix. The addition of complicated geometry and configuration, including a heterogeneous poral network will be implemented gradually.

The first phase of the study begins with categorizing the SiC matrix based on the overall influence of the pore network (porosity and pore size), which is determined by three methods to understand the origin of these variances. The second phase alters the thickness of the specimens rather than the slurry formulation to investigate the presence of a critical thickness at which some phenomena causing pore morphology led to a gradient of imbibition kinetics.

The third phase consist of a mixture of homogeneous and heterogeneous specimens with more complex geometry (P shape). This geometry comprise the morphology of a corner, as well as a convergent-divergent imbibition zone characterized by a transition zone. Phase four will have a simpler geometry but with layered layouts placed on top of each other. The fifth phase was completed as part of a master's thesis. A thorough examination of it is outside the scope of this study but the conclusions resulting from the simulation of macroscopic defects will be integrated in the final analysis to understand the effect of complex pore networks on capillary imbibition.

The numerical simulation is also done to show the capillary imbibition in two-dimensional geometry. The most essential aspect of this model is that it is solely dependent on the material and fluid characteristics. Predicting the imbibition kinetics does not require any thorough prior experience.

The following sections present the results of the characterization of the pore network of a SiC matrix in a more quantitative fashion, establishing the fundamental characterization based on the different techniques employed. The subsequent chapter combine the results with a more in-depth analysis, with the scope and domain of the discussion including all relevant parameters to develop an understanding of capillary imbibition through a porous SiC matrix based on the evolution of network complexity and the influences of different parameters.

In addition to experimental characterization, a dedicated simulation of the imbibition process based on the obtained parameters will be presented. This allows a correlation between the physical phenomena of imbibition and the simulation results. The simulation serves to determine one significant parameter that correlates imbibition with pore morphology in a three-dimensional representative volume: tortuosity. Its nature and its effect on the over-

all imbibition process must be precisely characterized to describe more precisely the pore network.

5.1 Impact of granular compaction on imbibition: phase I

This phase is distinguished by the qualities of defining the typical porosity for a rectangular homogenous SiC matrix, as well as validation of the fabrication process and comprehension of the phase's variation in microstructural properties. As previously stated, the three formulations considered in phase I are distinguished by the proportions of various elements such as SiC powder, binder, and dispersant. Due to proprietary concerns, precise quantities cannot be provided. For an overview of the samples in phase I, the characteristics of the three slurry formulations are given in Table 5.1.

Type	Concentration	pH range	Identification
A	20 % vol.	10 - 10.5	Standard compaction (SC)
B	20 % vol.	10 - 10.5	Low compaction (LC)
C	35 % vol.	9 - 10	High compaction (HC)

Table 5.1 Range of powder concentration with acceptable pH range for the fundamental formulations that form the basis of all coming configurations.

The three degrees of compaction (Table 5.1) generated three distinct poral networks, characterized by the level of porosity and pore size distribution, which established the basis for the corresponding porosity associated with each formulation. Formulations exhibiting greater compaction in the powder phase are expected to show lower overall porosity relative to those with lesser degrees of compactness.

The surface of slurry cast specimens after the de-molding has an uneven texture (Figure 5.1) due to using a specific textile tissue that facilitates the removal of consolidated SiC samples. Without this textile layer, the top surface of the consolidated SiC specimens might adhere to the metallic surface of the mold resulting in temporary agglomerates which turn very brittle as the drying of slurry takes place. The specimens were polished for surface leveling once they have completed heat treatment to bring a certain degree of surface uniformity.

The three experimental approaches to determine the porosity of rectangular SiC specimens have already been described in Section 4.4. The values that were obtained are given in Table 5.2. The results of porosity determined from the geometrical dimensions of the specimens were not retained due to the irregular contour of the specimens. This method is the least precise for determining porosity.

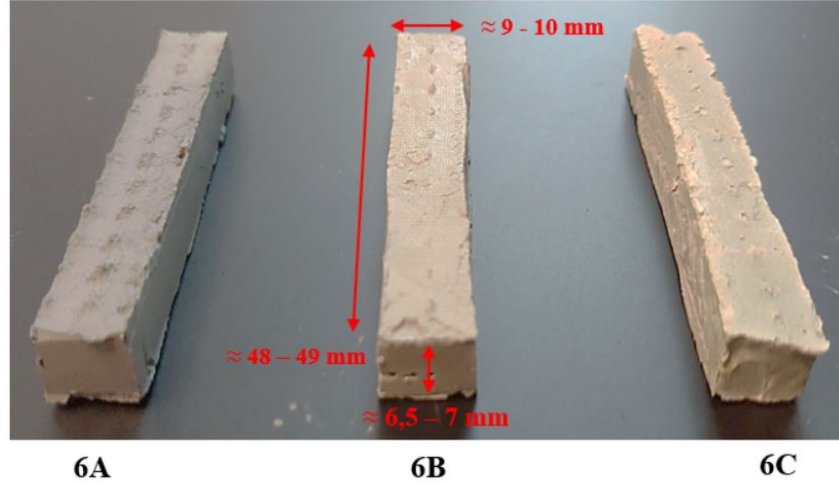


Figure 5.1 Typical three rectangular SiC matrix specimens that correspond to the three corresponding porosities of SiC matrix with two distinct families of SiC powders.

Formulation	Porosity ε (%)		Pore size d_{50} (nm)
	Buoyancy method [Twe]	Mercury intrusion [MIP]	[MIP]
6A	48.48 ± 0.10	42.47	409
6B	50.32 ± 0.80	45.85	434
6C	39.85 ± 0.85	35.48	474

Table 5.2 Comparison of porosity obtained by the two primary characterization techniques for determination of porosity : buoyancy (Twe) and mercury intrusion (MIP). A single specimen was analysed for MIP results.

The advantage of the triple weighing method (buoyancy) is the consideration of the whole volume of the specimens. It is then not sensitive to local variations in the porosity along the specimens. In addition, it does not depend on the measurement of specimen dimensions.

The observed disparity in porosity as a function of the employed techniques ranges from 15 to 20 %. Specifically, the discrepancy for triple weighing (buoyancy) is estimated to be between 9 and 12 %, while for MIP, it is projected to be within the range of 10 to 14 %. The utilization of the mercury intrusion technique is deemed to be a more complete approach as it gives information on pore size distribution. However, the triple weighing approach for the calculation of porosity is considered to be more pertinent since the complete microstructure participates in the pore network characterization while in the case of MIP, a smaller specimen is considered to be representative of the

The porosity determined by the buoyancy method is for all samples of all batches. How-

ever, due to equipment limitations to evaluate the porosity by MIP, only one representative specimen is selected from the batch, and samples were extracted from this representative specimen for characterization (Figure 5.2).

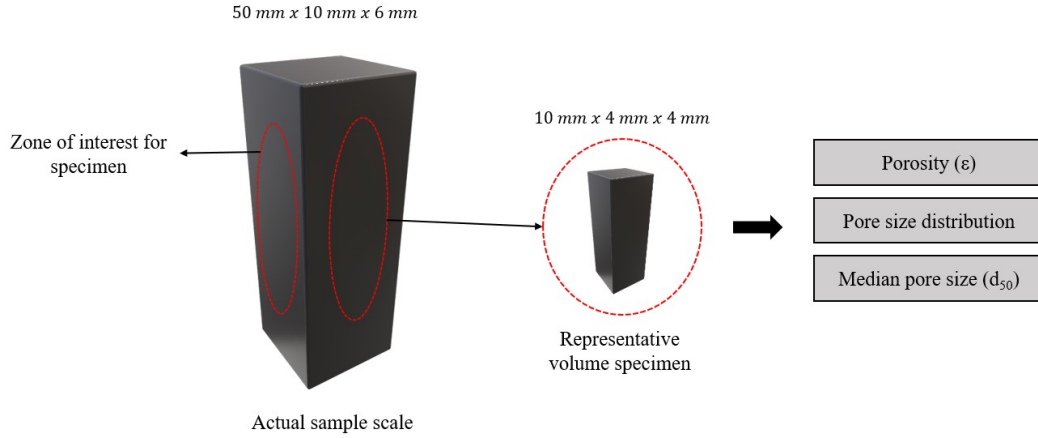


Figure 5.2 Schematic of the representative volume selection for MIP poral network analysis. The schematic shows the specimen extracted from the center and does not possess any surface zone matrix.

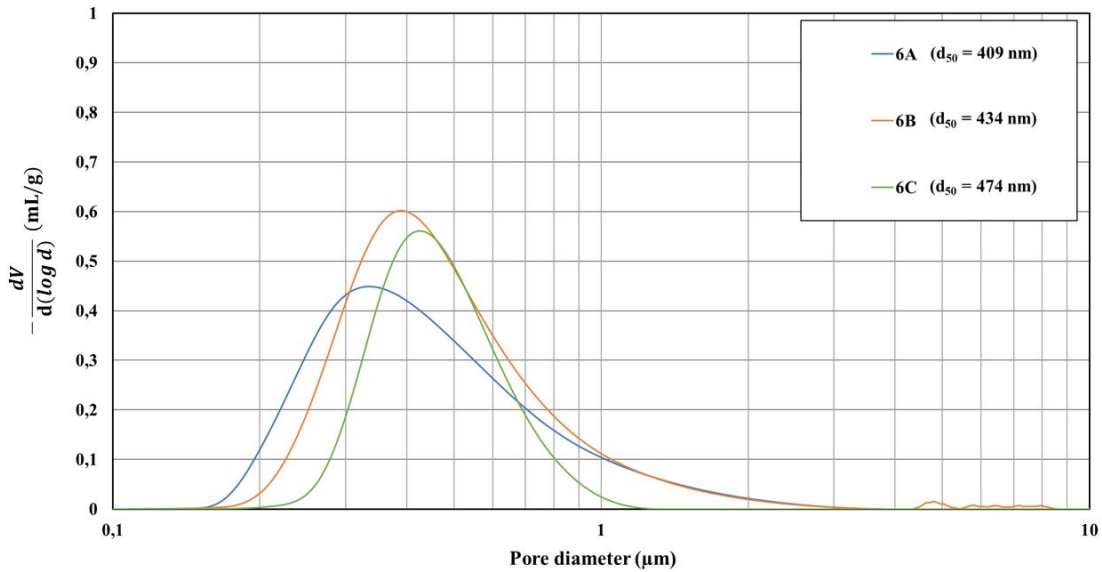


Figure 5.3 Microstructural characterization of porosity, pore size, and pore size distribution for the three formulations with uniform thickness and varied poral networks. The median pore size (d_{50}) is used to quantify the porous structure.

One crucial assumption in MIP is that the pore network of a smaller extracted sample is representative of the pore network of the larger actual specimen. The specimen extraction

site was chosen arbitrarily, while ensuring the absence of any pre-existing cracks within the designated area of interest. The results of MIP experiments on the three types of specimens are shown in Figure 5.3.

The matrix with the lowest porosity has a bigger median pore size. The lower porosity observed can be attributed to the increased compaction of the granular phase, leading to a corresponding increase in tortuosity. The pore size distribution provides the quantification of the scale of spatial porosities with their possible dispersion.

The median pore size d_{50} also quantifies the poral network that also constitutes a single morphological representation of the pore size. The median pore size for each formulation is obtained to be in a similar range and order which is understandable since the constituent SiC powder used for the formulations is of a similar type. Only the individual proportions of SiC powder and additives have been varied to obtain the three degrees of poral networks A, B, and C.

As a summary, even if the porosity ascertained through MIP gives a more precise value of porosity since it uses applied pressure to force mercury infiltration, because of the limitations in the access to the equipment and the local nature of the measurements, it was decided to prefer the buoyancy method to represent the porosity level of all the specimens in the present research work. The evaluation of porosity by triple weighing has the advantage to better represent the average value through all the specimens. However, for median pore size d_{50} and for illustrating the pore size distribution, the MIP method will be used.

5.1.1 Capillary rise experiments : uniform cross-section

The capillary rise tests are based on the Washburn technique to characterize the kinetics by the increase of infiltrated mass of fluid as a function of time.

The evaluation of the rate of mass increase permits to calculate the value of effective diameter d_{eff} corresponding to the diameter of a single capillary tube giving the same capillary flow kinetics as the porous material. This value of d_{eff} is determined experimentally from capillary rise experiments with the tracking of mass as described in Section 4.3.2. The results for the three types of specimen formulation of phase I are illustrated in Figure 5.4. The capillary-induced imbibition curves (Figure 5.5) present the comparative kinetics of the three microstructures. The evaluation of d_{eff} for the three types of specimens comes from the slope of the straight lines for the major part of imbibition. The imbibition curve is obtained by determining the total infiltrated mass of hexadecane minus the meniscus generated at the beginning of the imbibition.

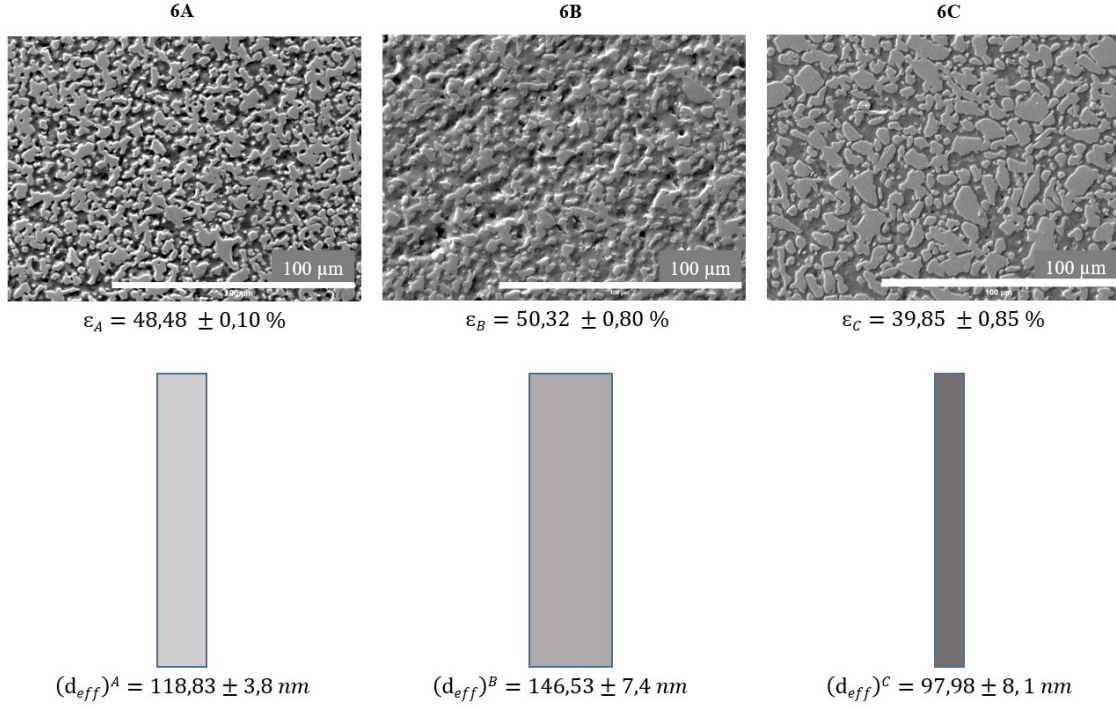


Figure 5.4 SEM images of the two-dimensional microstructure which have been extracted from the central/middle zone of the SiC matrix that are initially represented as single capillary tube that is defined by its effective diameter (d_{eff}).

From Figure 5.5, one can denote that type B specimens exhibit the highest imbibition rate, whereas the microstructure of type C specimens displays the lowest imbibition rate. Upon analyzing the microstructural parameters from Table 5.2 and Figure 5.4, it is clear that the combination of pore characteristics of specimen B led to the largest value of effective diameter as compared to specimens C leading to the smallest value of d_{eff} .

The initial methodology for elucidating the imbibition dynamics in a matrix with a uniform cross-section involves an explanation grounded on the concept of the theoretical effective diameter. The quantification of the microstructural consequences of a single capillary tube d_{eff} . The concept of higher effective diameter comprises a range of key morphological features that have a significant impact on the dynamics of imbibition. A larger effective diameter results in reduced viscosity losses for the flowing fluid, leading to enhanced imbibition rates.

From these results, it seems that a larger value of effective diameter generates lower capillary pressure since the effective diameter is considered to possess the combined effect of the microstructural parameters on the poral network, therefore the effect on the reduction of resistance to the flow becomes dominant. The behavior of capillary flow in specimens of type A lies between that of type B and type C. It is noteworthy that the Washburn effective

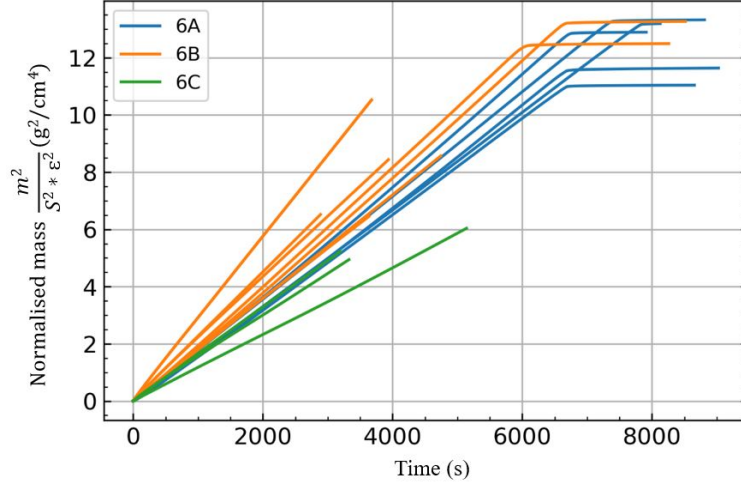


Figure 5.5 The normalized imbibition rate for porous SiC matrix with the inclusion of cross-sectional porosity ϵ . The three microstructures present similar dispersion between the different batches and within the same batch of specimens.

diameter is not representative of direct pore structure metrics.

However, by considering the Richards approach with the definition of the absolute permeability (Equation 2.22), the coherence of experimental results of capillary kinetics could be better explained in relation with the value of permeability. If the values of porosity and d_{50} are known with a certain precision for the three types of pore network, for the moment, the value of tortuosity is not known.

The identification of the poral network in the displacement of the gas phase (air) by the liquid wetting phase (hexadecane) is made possible by the quantitative characterization of the poral network. This is accomplished through hydraulic conductivity, which is a result of the poral factors that affect the dynamics of imbibition. By using the Van Genuchten function to fit the intrusion curve for mercury intrusion porosimetry, the hydraulic conductivity may be calculated.

The Van Genuchten function has two empirical parameters α and n that have to be determined by an experimental curve fit from the mercury intrusion experiment, as shown in Figure 5.6 and Figure 5.7. It was necessary to set the value of α (kPa^{-1}) to obtain the value of n which characterizes the slope in the transition. However, for the numerical simulation purpose with FlexPDE tool, the value of α is determined by taking the inverse of capillary pressure that is related with the pore size and the surface tension (Young-Laplace Equation 2.6).

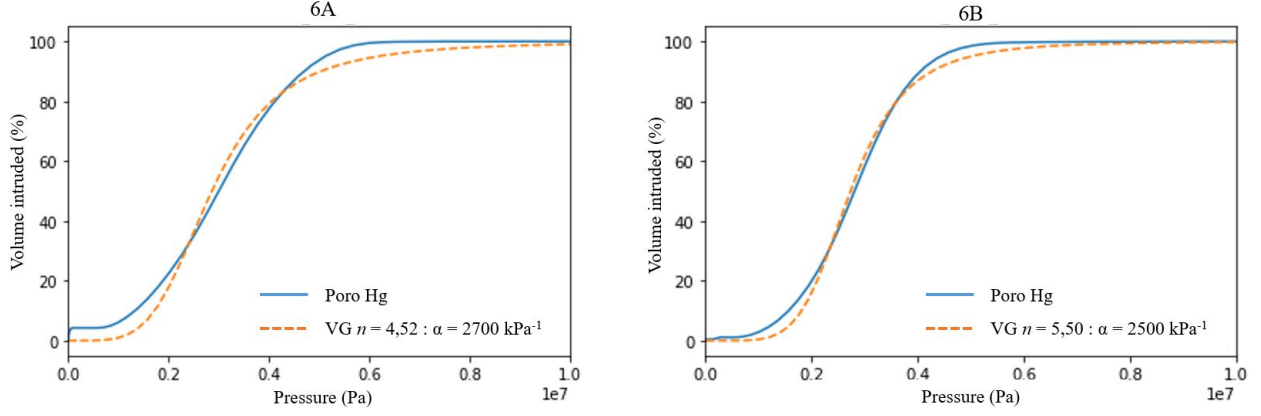


Figure 5.6 Fitting between the percentage intrusion of mercury with the Van Genuchten function to determine the empirical parameter to be used further in the characterization of imbibition dynamics for specimens of types A and B.

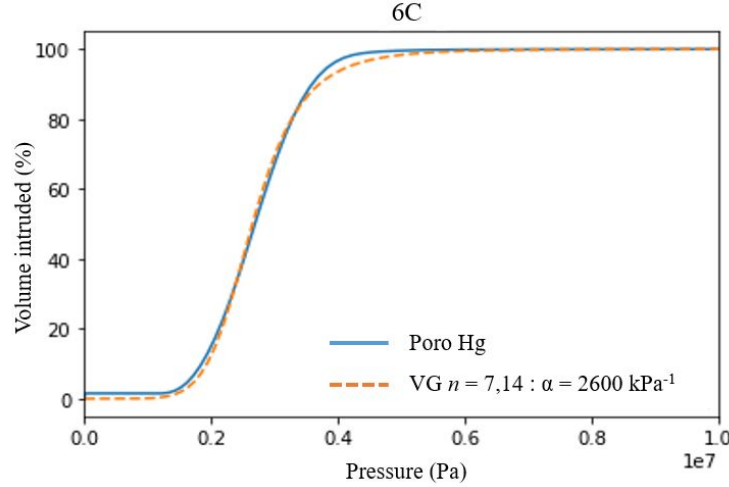


Figure 5.7 Fitting between the percentage intrusion of mercury with the Van Genuchten function to determine the empirical parameter to be used further in the characterization of imbibition dynamics for specimen of type C.

5.1.2 Simulation of capillary imbibition

For the confirmation of the imbibition phenomena in porous SiC matrix, the FlexPDE software has been applied to reproduce the capillary flow phenomenon that might offer an additional explanation of the effect of morphological parameters connected to the pores. This model is based on the resolution of the Richards' partial differential equation (Equation 2.24) by the finite element method. This model does not take into account the effect of gravity since the other forces (viscous, inertial, and capillary) are significantly more important in the imbibition phenomena for the SiC specimens studied in the present thesis.

The methodology to launch the application involves establishing boundary conditions for the macroscopic specimen contour. In addition, it is necessary to specify porous material characteristics (porosity, median pore size, pore size distribution characterized by Van Genuchten parameters) and capillary fluid properties (viscosity, density, wetting angle, surface tension).

Another parameter that is very important is the tortuosity τ , that unfortunately cannot be experimentally evaluated. In our simulation approach, this parameter will be set in order to obtain a good correlation of mass increment (imbibition rate) between the experimental mass tracking curve of capillary rise and the simulated mass tracking calculated by FlexPDE. All the input data concerning the characteristics of porous media are given in Table 5.3. The properties of the fluid (hexadecane) were given previously in Table 4.6.

Specimen	Porosity ε (%)	Median pore size d_{50} (nm)	Van Genuchten n
6A	48.48	409	4.52
6B	50.32	434	5.50
6C	39.85	474	7.14

Table 5.3 Parameters that are utilised for the initialisation of morphological properties over the defined geometry.

After running FlexPDE by considering the properties of hexadecane at room temperature and the pore network characteristics (porosity determined by triple weighing and d_{50} by MIP) specific to each of the three types of specimen formulation, the comparison of experimental impregnated fluid mass and simulated one is presented in Figure 5.8.

The value of the tortuosity τ for each case that was necessary to impose to obtain a good fit is given above each graph. The quality of the fit between the simulation and the experimental curve can be judged by the superposition of the curves and the values of d_{eff} resulting from both approaches.

As described in Section 2.7.1, the value of tortuosity for a given pore network is mostly impossible to determine precisely. However, in our present case, the values that were determined to obtain a good fit between experimental mass measurement and numerical simulation through FlexPDE make some sense. For specimens 6A and 6B, the SiC powder that was used for slurry preparation is identical in both cases. Therefore the variation is fundamentally due to different pore sizes.

The formulation method however differs which results in a slightly higher porosity and larger median pore size for type B, giving lower resistance to capillary flow and lower tortuosity than that for type A specimens. For specimen 6C, the SiC powder was not the same as that

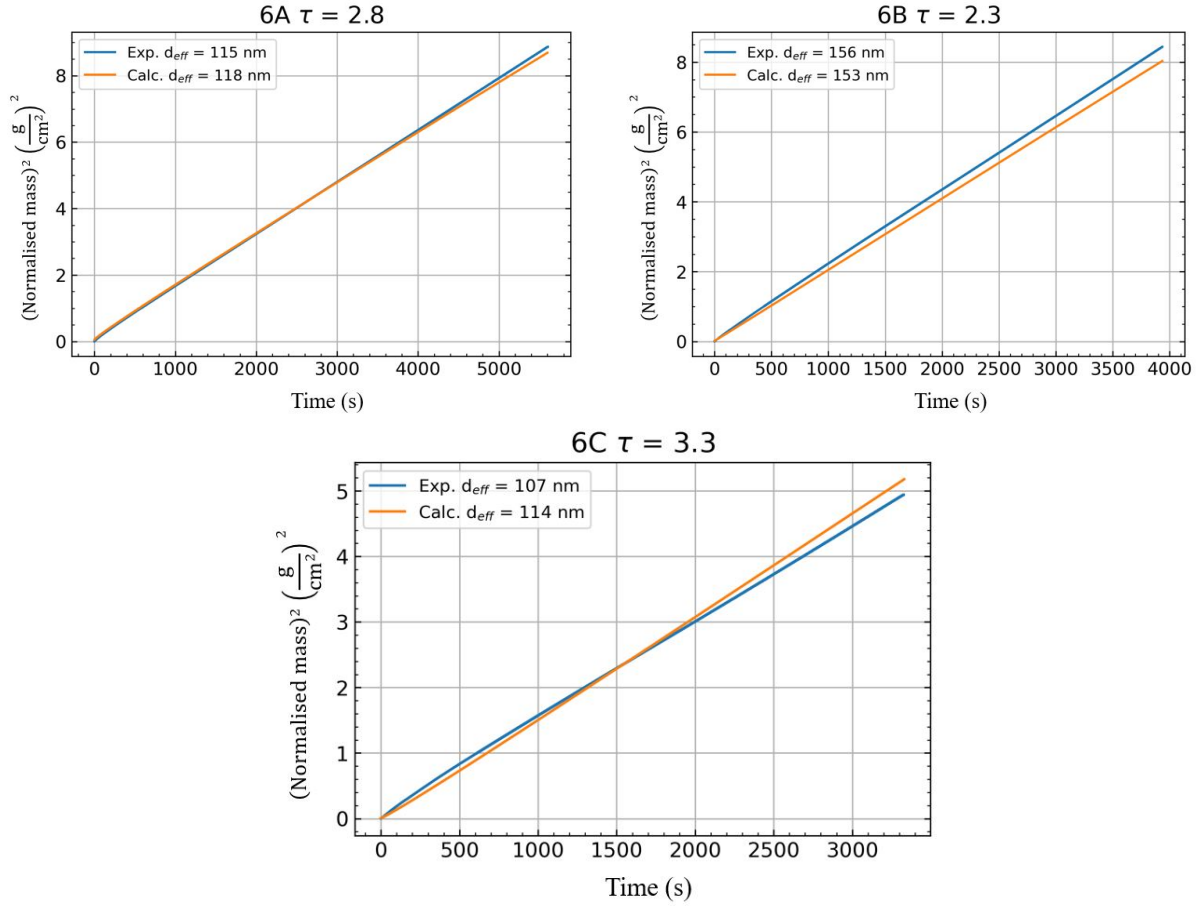


Figure 5.8 Comparison of normalised mass evolution between experiments and simulations using Richards approach. The value of tortuosity τ is calibrated to get a good correlation. For 6A: $\varepsilon = 48.5 \%$, $d_{50} = 409 \text{ nm}$ and $\tau = 2.8$. For 6B: $\varepsilon = 50.3 \%$, $d_{50} = 434 \text{ nm}$ and $\tau = 2.3$. For 6C: $\varepsilon = 39.8 \%$, $d_{50} = 474 \text{ nm}$ and $\tau = 3.3$.

used for 6A and 6B.

As seen in Figure 5.4, the SiC particle size distribution for type C is wider. When the void between larger particles is filled with smaller particles, this tends to give lower porosity and a more tortuous path for capillary flow, resulting in a higher value of tortuosity. This can also explain why type C specimens have slower capillary rise kinetics compared to types A and B. Now that we have an evaluation of the tortuosity for each type of pore network, it is possible to verify that the values of permeabilities calculated from Equation 2.22 are in good agreement with the experimental ranking of the capillary rise kinetics from B, A to C in decreasing order.

To evaluate the contribution of pore network characteristics on the simulation of capillary flow, a median pore size ($d_{50} = 400 \text{ nm}$) of arbitrary value is selected to simulate the imbi-

bition across the three formulations. All other parameters are utilized in a manner that is specific to each particular type. The entry parameters selected for this first round of simulation are given in Table 5.4. The graphical results for the saturation profile along the bar specimens after 3000 s of simulated imbibition are shown in Figure 5.9.

Specimen	ε (%)	d_{50} (nm)	τ (-)	Time (s)	d_{50} for sim (nm)	Van Genuchten n
6A	48.48	409	2.8	3000	400	4.52
6B	50.32	434	2.3	3000	400	5.55
6C	39.85	474	3.3	3000	400	7.14

Table 5.4 The parameters used for simulation to determine the effect of porosity on capillary rise for a given d_{50} .

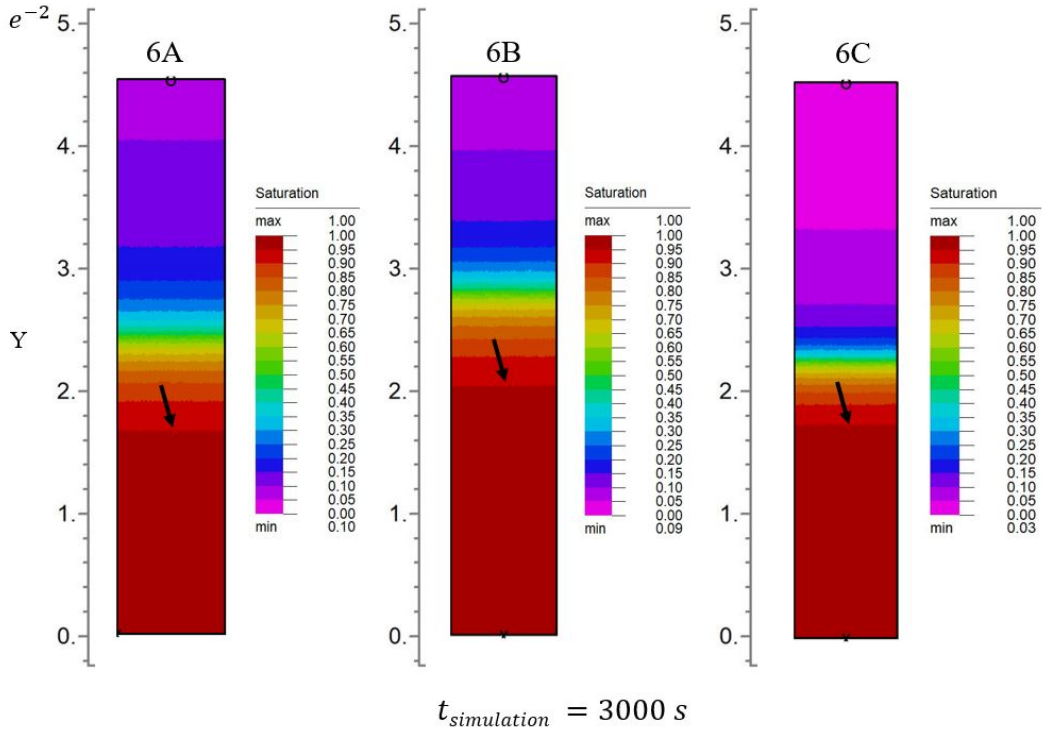


Figure 5.9 The simulation for the homogeneous specimen of Phase I to identify the dominant parameter. The median pore size (d_{50}) is kept constant at 400 nm. Color scale indicates the level of saturation s . The black arrow indicates the position of saturation level = 100 %.

The advancement of the flow front in relation to full saturation exhibits varying degrees along the specimens in the direction of imbibition (from bottom to top). Given the uniform thickness of all specimens, it can be inferred that the imbibition profiles remain the same through the thickness. Assuming porosity as the primary parameter affecting the imbibition

rate (since median pore size is imposed to be equal for the three formulations), it can be inferred that the specimen possessing the highest porosity and the lowest tortuosity would demonstrate the most rapid advancement. This makes sense because constant d_{50} means constant capillary pressure. In addition, Equation 2.22 shows that permeability is proportional to the porosity and median pore size, so the capillary phenomenon in porous media could be relate to the permeability value of the material.

For more porous specimens, like type B in the present case, it means that the tubular channels are more numerous, leading to higher mass gain during imbibition. Also, since the tortuosity is lower for type B, this means that the resistance to capillary flow is lower, enhancing then the capillary flow kinetics. However, it seems more difficult, with similar arguments, to explain why the flow kinetics in specimens A and C are not so different by judging from the complete saturation $s = 100$ % level. Nevertheless, the saturation gradient in specimen C is much more contracted as compared to other scenarios, probably indicative of the higher value of the Van Genuchten parameter n that was used for the simulation.

A second scenario was considered for simulating the effect of the pore network on capillary flow. This time, the approach consisted in selecting the porosity as the average value (43 %) obtained from the triple weighing of all three types of specimens. The input median pore size values for each type correspond to the experimental measures through MIP. The entry parameters selected for this second round of simulation are given in Table 5.5. The graphical results for the saturation profile along the bar specimens after 3000 s of simulated imbibition are shown in Figure 5.10.

Specimen	ε for sim (%)	d_{50} (nm)	τ (-)	Time (s)	Van Genuchten n
6A	43	409	2.8	3000	4.52
6B	43	434	2.3	3000	5.55
6C	43	474	3.3	3000	7.14

Table 5.5 The parameters used for simulation to determine the effect of median pore size on the capillary rise for a given porosity ε .

For this second scenario, it seems that there is not a clear relationship between the capillary kinetics and the median pore size. This is probably due to the opposing effects of capillary pressure and resistance to the flow. Smaller pore size generates higher capillary pressure but also higher viscous resistance to the flow. For that reason, the saturation profiles in the three types of specimens are very similar to those obtained in the first scenario where the median pore size was the same and the porosity different from one specimen type to the other. Again, the effect of tortuosity (different for the three types of specimens) seems to be determinant,

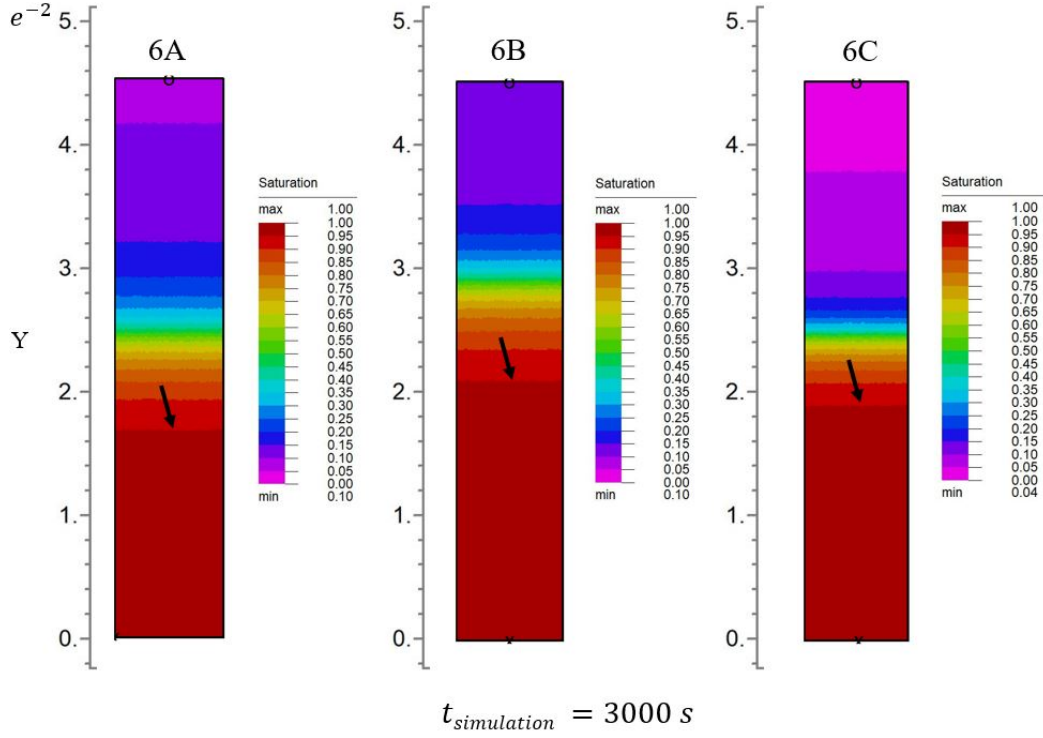


Figure 5.10 The simulation for the homogeneous specimen of Phase I where the porosity (ε) is kept constant at 43 %. Color scale indicates the level of saturation s . The black arrow indicates the position of saturation level = 100 %.

at least for the establishment of saturation gradient along the specimens. Even if the value of permeability is proportional to the square of d_{50} (Equation 2.22), the slight difference in the median pore size from one type of poral network to the other tends to give a value of d_{50}^2/τ in the same order as the kinetics classification shown in Figure 5.10.

The analysis of simulation outcomes for the two previous scenarios featuring consistent median pore size and porosity yields valuable findings regarding the factors that exert a more prominent influence on the capillary imbibition of SiC porous specimens. It appears that all three porous material characteristics (porosity, median pore size and tortuosity), taken individually or in combination, play an important role in the development of capillary flow kinetics. It would have been interesting to have a larger gap between the values of these parameters from one type of specimen to the other to reveal more clearly their importance.

Nevertheless, when the behavior of heterogeneous materials with different pore network characteristics will be considered in phases III and IV, even slight differences in porosity or median pore size would have a clear impact on capillary impregnation profiles.

When the mass tracking and height tracking for the capillary rise are compared, it is nec-

essary to establish a clear determination of the saturation level corresponding to the flow fronts position that could be detected at the lateral surface of the specimens. The contrast between the height approach and mass approach may offer valuable insights into the potential configuration of the diffuse flow front for the three distinct cases.

This is illustrated for example in Figure 5.11 where it can be seen that the evaluation of mass gain in specimen 6A from the position of the flow front at the surface is always lower than the continuous mass gain measured experimentally during capillary rise experiments. This systematic under-evaluation is not due to uncertainties in the measures. As we will see later, it can be explained by the volume flow front evolving faster than the surface flow front, causing a higher mass recorded from the mass tracking compared to that evaluated from height tracking.

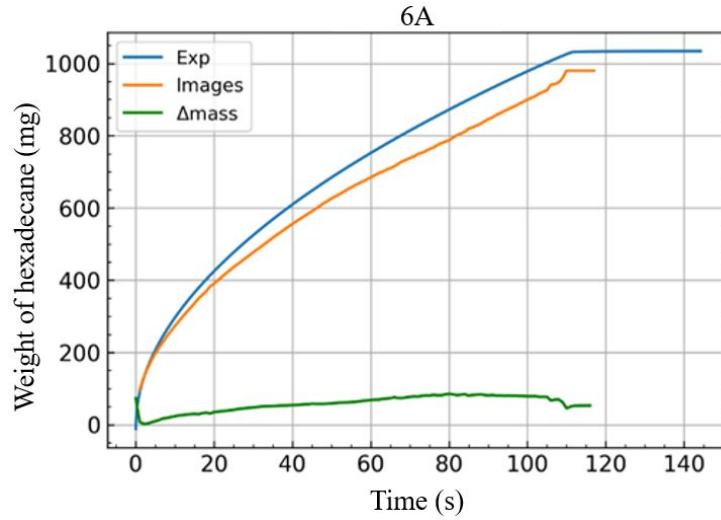


Figure 5.11 Difference between the infiltrated mass evaluated from the two approaches (mass and height).

An important assumption is being made concerning the advancing flow front, which supposes that the flow front that is observable at the surface is indicative of complete saturation, encompassing the volume that is covered by the diffuse flow front. In this study, the surface flow fronts resulting from capillary rise experiments are compared to the distribution of saturation given by FlexPDE by using the pore network characteristics measured experimentally (Figure 5.12).

There is a saturation gradient predicted from the simulation. However, the level of complete saturation would not correspond to the visible surface flow front, but there should be a range of degrees of saturation for which the emergence of the surface flow front occurs that is visible without any enhancements.

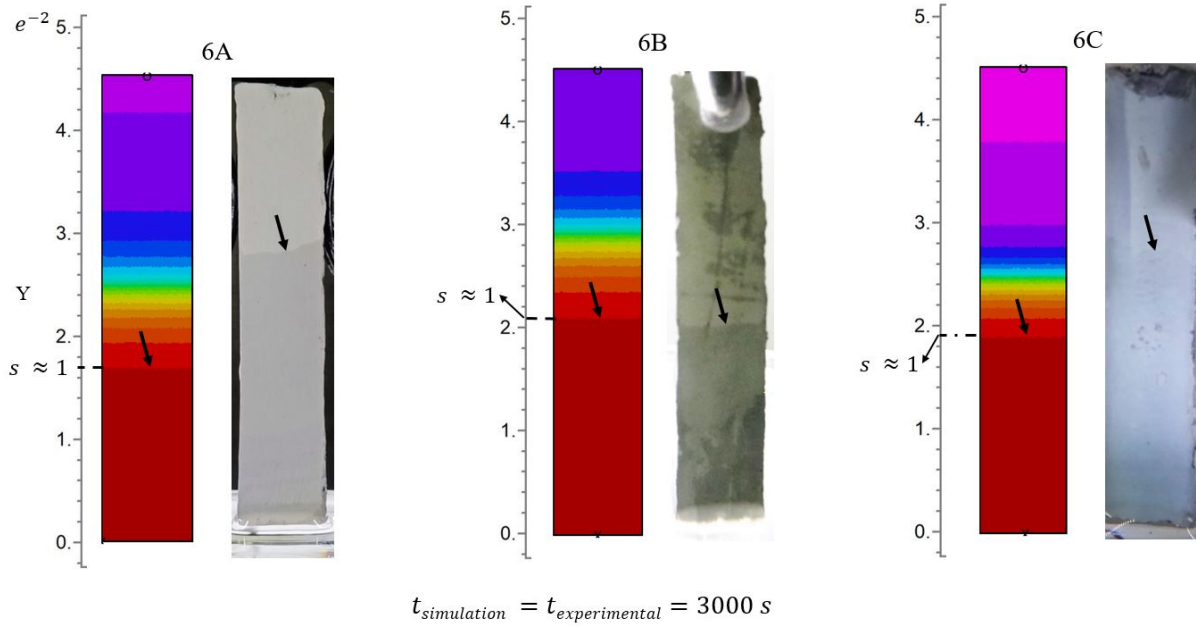


Figure 5.12 Comparison between simulations and experiments at $t = 3000$ s. The black arrows on color plots indicate a saturation level of 100 % while the ones on the experimental photos indicate the flow front as detected on the surface. The values entered for the simulations are the following: 6A: $\varepsilon = 48.5$ %, $d_{50} = 409$ nm, $\tau = 2.8$; for 6B: $\varepsilon = 50.3$ %, $d_{50} = 434$ nm, $\tau = 2.3$; for 6C: $\varepsilon = 39.8$ %, $d_{50} = 474$ nm, $\tau = 3.3$.

It becomes necessary to investigate the degree of saturation between the level at the surface that is visible to the naked eye and the one predicted by FlexPDE. For this, a comparison of the experimentally detected height corresponding to different saturation levels was made. The two curves are plotted together on the same graph for each formulation to identify the level of saturation corresponding to the position of the front (Figure 5.13).

The comparison of the difference between the increment of height based on image processing and experimental methods gives the range of the threshold level of saturation to be between 40 and 50 percent as can be seen in Figure 5.13 for formulations A and B while this threshold presents a very lower value for type C formulation.

This could be due to the fact that the visualization of the surface flow front for C-type formulation is comparatively difficult and has a high susceptibility to error. The result for 6C, although quite different from those obtained for 6A and 6B, can provide evidence that there is a saturation gradient that is developed at the surface where the diffuse flow front progresses ahead of the flow front that corresponds to the visible front at the surface.

A comparable degree of saturation range has been selected for A and B, as the SiC powder utilized in the production of the specimens is identical, with only a variation in the proportion

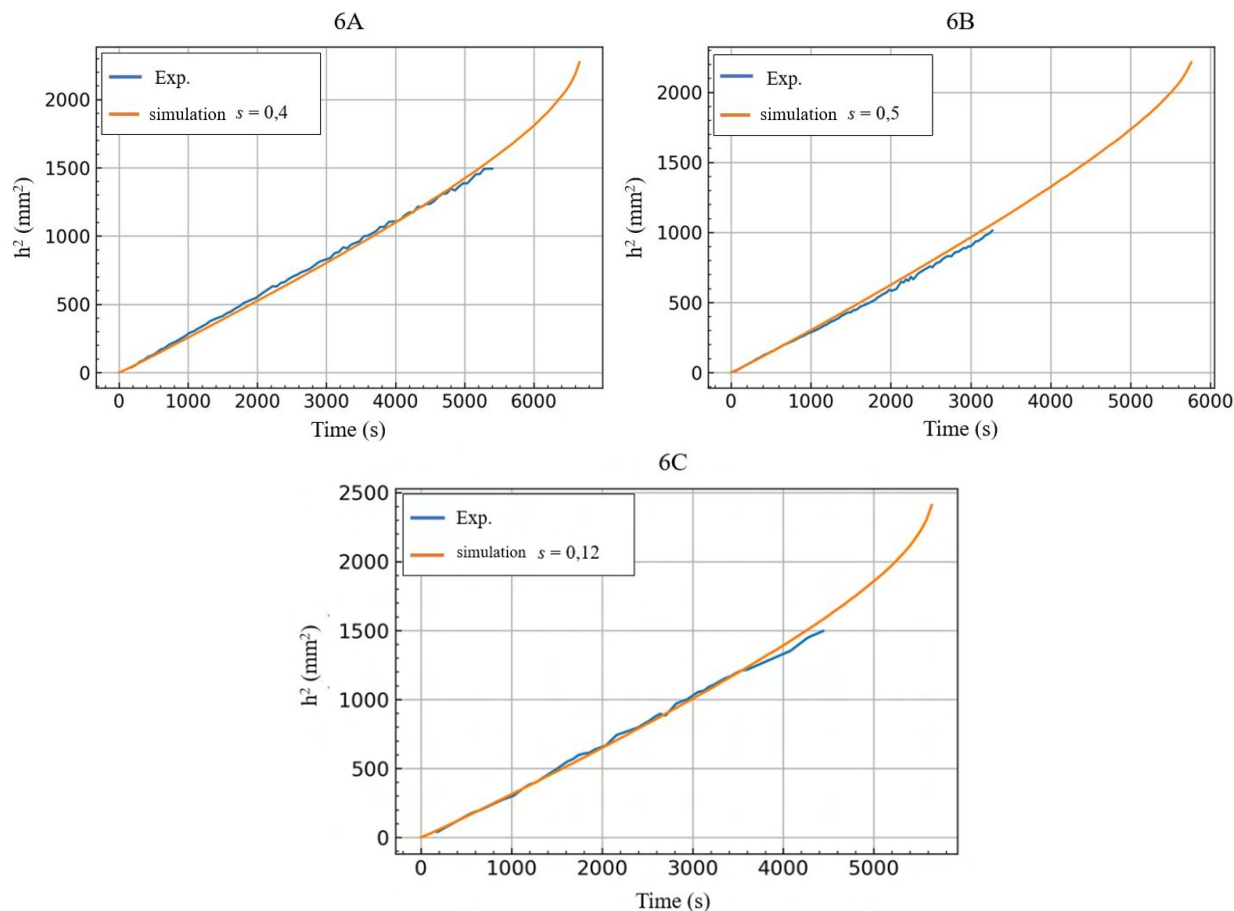


Figure 5.13 Comparison between simulations and experiments of the surface flow front height h considering an iso-value of saturation as flow front position: formulation A: 40 %, formulation B: 50 %, formulation C: 12 %.

of other additives. The utilization of an alternative powder in the C variant results in a modification of the granular phase morphology. Additionally, the pore network for 6C specimens exhibits distinct morphological characteristics compared to those observed in the A and B variants (see Figure 5.4).

The dispersion of pores in space, along with their intricate and stochastic morphology, resulting in significantly higher tortuosity as determined from simulation, may have an impact on the advancement of hexadecane. The SiC matrix presents a greater level of spatial complexity when attempting to conceptualize its poral network based on the imbibition dynamics. Hence, it is imperative to examine a three-dimensional representation of the advancing flow front in order to establish the imbibition kinetics within a SiC matrix.

The three-dimensional visualization of the flow front is made possible by means of interrupted tests with *exo*-DCPD with a tin salt dopant that shows contrast where resin impregnates the

porous material. The observation of a partially impregnated SiC matrix under tomography reveals intriguing features regarding the proposed hypothesis of two discrete flow fronts at the surface and interior of specimens. This approach will differentiate the surface flow front (SFF) and the volumetric flow front (VFF) as can be observed in 3D by tomography. As shown in Figure 5.14, it appears that the flow front advances more rapidly along the central longitudinal axis of the specimens (from bottom to top).

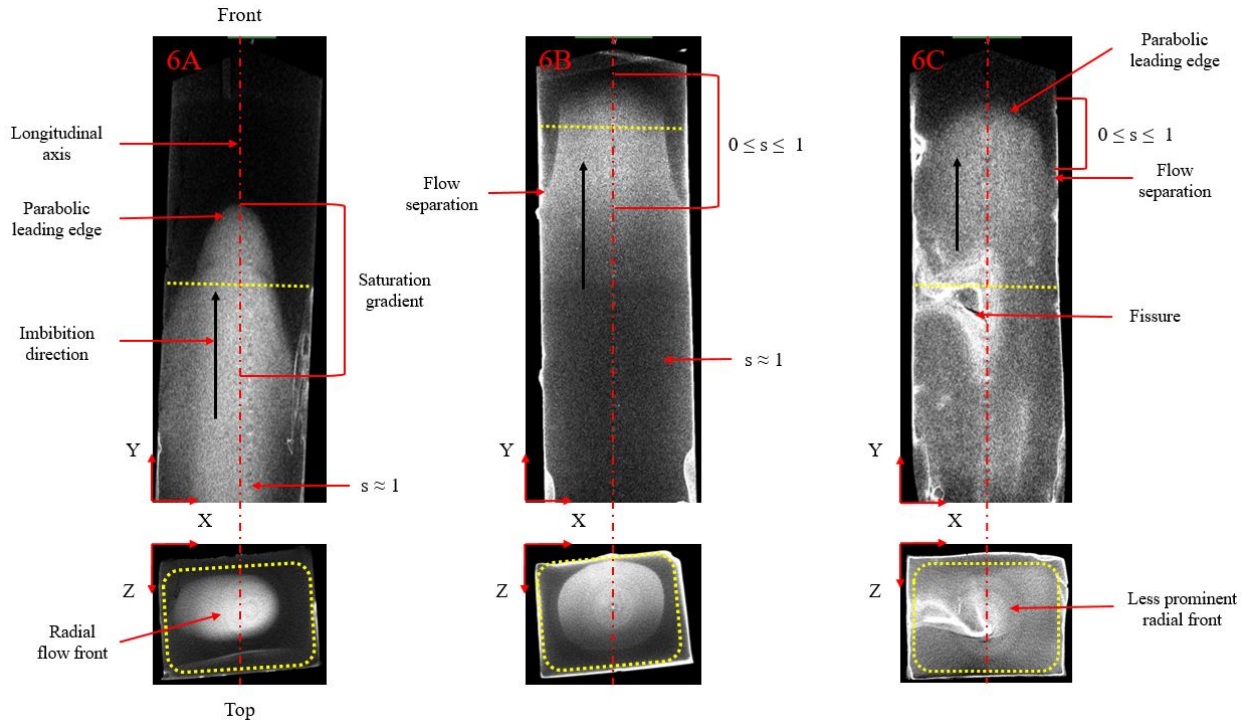


Figure 5.14 Three-dimensional visualization for the three specimens obtained by microtomography after interrupted tests. The yellow demarcation shows the sectional view of the SiC matrix

When viewed from above (top view), there is also evidence of radial extension of the flow front. Using the correlation between surface flow fronts that have been determined to be 40 % for A, 50 % for B, and 12 % for C, the threshold limit for saturation gradient appears to be influenced by the overall porosity and pore morphology. The microstructure of the A, B, and C formulations differs significantly. C has larger granular coagulation, whereas A and B have very similar microstructures in terms of morphology, spatial distribution, and porosity level, with the exception of the average pore size.

A point of flow separation is observed, beyond which the fluid predominantly advances within the interior of SiC matrix. Consequently, the surface flow front (SFF) would trail the volume flow front (VFF), explaining then the under-evaluation of impregnated liquid mass deter-

mined from SFF. The correlation between the advancement of the volume flow front and the surface flow front seems to present compelling evidence to contemplate the saturation threshold limit for the volume flow front, beyond which the surface flow front becomes perceptible.

The examination of the evolution of volume flow front in the SiC matrix from Figure 5.14 reveals a distinct parabolic flowfront that is well-defined and exhibits a noticeable difference between the surface and the inside of the matrix. The occurrence of parabolic flow fronts can be ascribed to the disparity in microstructure between the outermost layer and the inner core of the SiC matrix. The observed phenomenon may be attributed to the thermal treatment of porous SiC matrix samples, resulting in the fusion of granular phases. This fusion is influenced by many process factors, including temperature, ramp rate, and chamber environment.

5.1.3 Concluding remarks for phase I

The uniform-thickness specimens for phase I that represent three distinct porosities and microstructures provide an initial basis for the establishment of fundamental principles that aid in the comprehension of the capillary imbibition of porous SiC matrix. The protocol for the fabrication of specimens has been validated for its reproducibility. The specimens fabricated present a small dispersion within the same batch. This is expected considering the fabrication conditions that are not uniform for every round of slurry preparation and injection.

From the results of capillary rise experiments in phase I, it appears that there is no clear dominance of one microstructural parameter with respect to the others. The median pore size, the porosity, and the tortuosity do all seem to play an important role in the imbibition rate. However, the overall capillary kinetics behavior of the three formulations is clearly different, as expected for this first phase.

An interesting aspect of capillary flow characterization through X-ray computed tomography is the illustration of different behavior of capillary kinetics from the surface of the specimen to its center. The surface flow front (SFF) tends in most cases to progress more slowly than in the center of the specimen where the volumetric flow front (VFF) seen in 3D in tomography forms a parabolic shape. This aspect will be described in more detail in phase II (Section 5.2) where the effect of the thickness of the specimen is investigated.

No matter what method is used for capillary imbibition characterization (weight or height tracking), the capillary kinetics can be described by a Washburn law. This characterization approach can lead to the determination of an effective pore size d_{eff} that is a good indicator of the capillary kinetics, even if it does not have physical meaning with actual pore network

metrics.

The approach consisting in the simulation of the capillary flow by solving the Richards equation through FlexPDE leads to coherent results based on the porous material characteristics (porosity, median pore size, tortuosity) and fluid properties. The capillary kinetics obtained by FlexPDE are in good agreement with Washburn law where the square of the mass (or height) varies linearly with time.

When comparing the experimental results of capillary flow progression (mass tracking, height tracking, interrupted tests with *exo*-DCPD) with the result of numerical simulation with FlexPDE, there is still a phenomenon that has to be clarified concerning the gradient of saturation of impregnation along the flow front. Whether the flow front line that is observed by eyes on the surface of the specimens corresponds or not to the abrupt transition from 100 to 0 % saturation has to be investigated in more detail and will be discussed in Chapter 6. However, the 3D images obtained from micro-tomography seems to indicate that the flow front is not diffuse but abrupt in terms of saturation gradient.

5.2 Impact of thickness on capillary imbibition: phase II

This phase encompasses variation in the thickness of the SiC specimens without changing the formulation, which was selected to be of type A. The nominal thicknesses for the different specimens were 3 mm (3A), 6 mm (6A), and 9 mm (9A).

Figure 5.15 shows the typical specimens after slurry cast, drying, and heat treatment. The overall integrity of fabricated specimens is very low before heat treatment. This changes significantly with high-temperature heat treatment. The fabricated specimens have some surface irregularities that are due to the tissue that is placed to ease the removal of specimens from the mold. There is good control over the final thickness that is attained by regular injection with the same protocol as for phase I but with a modified PTFE mask.

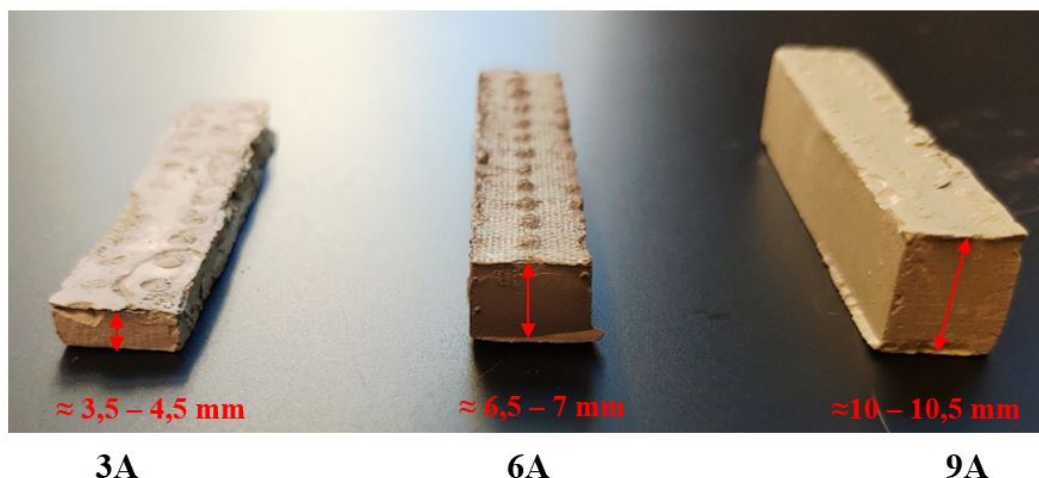


Figure 5.15 Typical surface and respective thickness range for the specimen of phase II. They incorporate a uniform cross-section attributed to the rectangular geometry of the SiC matrix.

5.2.1 Characterization of poral network

The characterization of the microstructure for phase II begins with the determination of median pore size diameter d_{50} (MIP) and porosity obtained by the buoyancy method since it comprises the complete volume of the matrix. The main results for this characterization are given in Table 5.6. Similarly to what was obtained for phase I, the porosity evaluated by MIP is smaller than the ones obtained from triple weighing.

Specimen	Porosity (%)		Pore size d_{50} (nm)
	Bouyancy method [Twe]	Mercury intrusion [MIP]	[MIP]
3A	45.14 ± 0.21	42.77	390
6A	48.48 ± 0.10	42.47	409
9A	45.17 ± 0.08	42.25	321

Table 5.6 Pore network parameters obtained by buoyancy and mercury intrusion methods for determination of porosity and pore size for phase II.

Since the measures by triple weighing are done on the whole specimens, it is believed that the porosity results are more representative of the response of the specimens during capillary rise experiments. By keeping the same slurry formulation for this phase, it was expected that the pore network would be the same from one specimen to the other. It appeared that it was not the case.

The median pore size shows a similar range for all specimens (Figure 5.16), within the experimental dispersion associated with the fabrication process. The 6A specimens were

created as part of phase I and the results for 6A have been included in phase II. 3A and 9A specimens have been created as part of the same injection round, with the exception of a variation in thickness for the specimens.

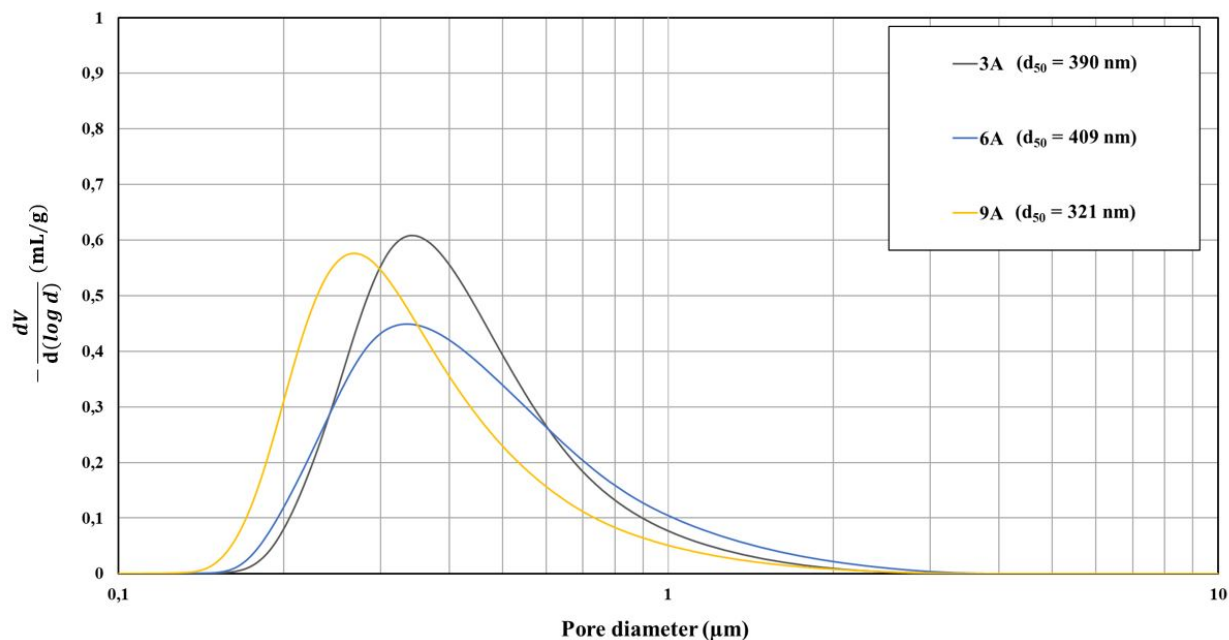


Figure 5.16 Combined microstructural characterization for a single formulation of different thicknesses shows the variation in median pore size and pore size distribution.

Considering the typical standard deviation for the evaluation of d_{50} by MIP, it appears that the gap between specimens 3A, 6A, and 9A is significant and difficult to be explained since the three thicknesses were supposed to be identical pore structure (same formulation). The capillary rise experiments described further reveal that different thicknesses provide some evidence of a critical threshold limit of thickness above or below which the imbibition dynamics change even for similar formulations.

For that reason, a second round of experiments was carried out to identify a variation in the pore structure through the thickness of the specimens. For thicker specimens (6A and 9A), samples for MIP were extracted from two different zones, near the surface of the specimen and in the center of the specimens, as shown in Figure 5.17.

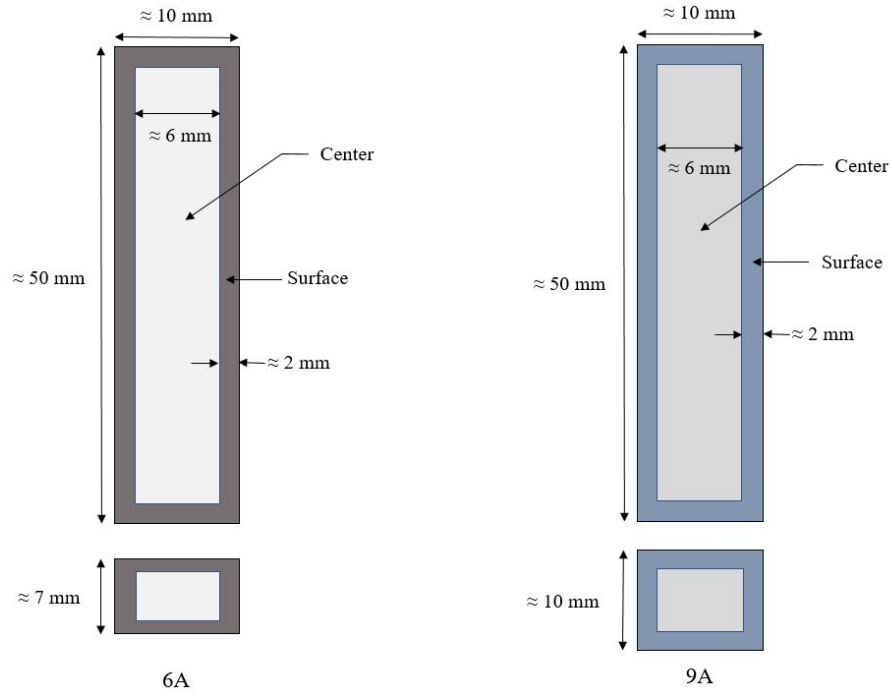


Figure 5.17 Identification of the two zones defined as central and surface for microstructure characterization of 6 and 9 mm specimens.

The results of these experiments are shown in Figures 5.18 and 5.19. As further proposed in this section, the influence of heat treatment on the spatial heterogeneity should be exacerbated with increasing material thickness, as temperature gradients are more significant in thicker materials, with temperature being higher at the surface. The results in Figures 5.18 and 5.19 do not show this clearly. Again it is important to remind that local MIP measurements have inherent dispersion and are not fully representative of the whole material.

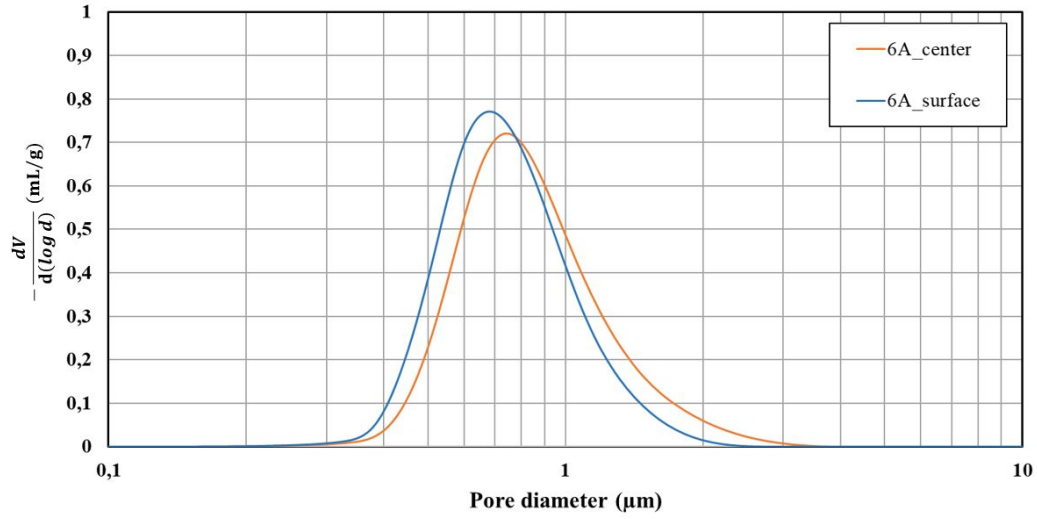


Figure 5.18 Difference in the pore size distribution (MIP) taken from the surface and at the center of specimen 6A.

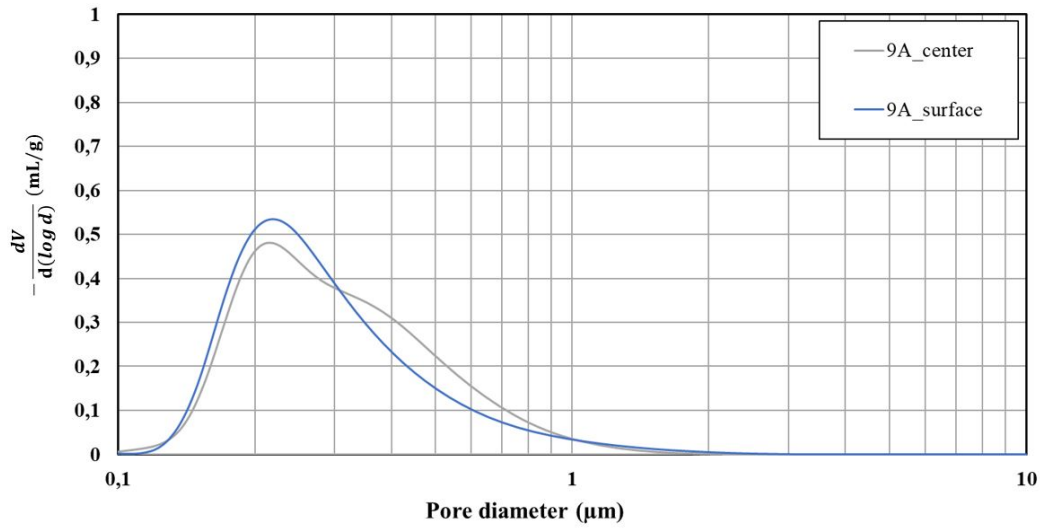


Figure 5.19 Difference in the pore size distribution (MIP) taken from the surface and at the center of specimen 9A.

The results for median pore size (d_{50}) and porosity evaluated locally by MIP are summarized in Table 5.7. In spite of the fact that the microscopic examination of the microstructures and the local MIP measurements do not reveal noticeable differences from the surface to the center of the specimens, a slight gradient of d_{50} will be introduced in FlexPDE to simulate the capillary imbibition to validate the generation of parabolic front through the matrix. This microstructure gradient could reasonably be explained by differences in heat treatment

temperatures from the surface to the center of the specimens.

Specimen	Median pore size d_{50} [MIP] (nm)		Porosity ε [MIP] (%)	
	Center	Surface	Center	Surface
6A	392	486	47.10	47.03
9A	289	253	41.10	42.10

Table 5.7 MIP poral network characterization from specimens 6A and 9A at the center and at the surface.

5.2.2 Capillary rise experiments: continuous with n-hexadecane

The capillary rise experiments were performed with hexadecane to characterize the kinetics of the capillary phenomenon in a SiC matrix with varying thicknesses. The results shown in Figure 5.20 give an indication of the kinetics of imbibition in specimens of different thicknesses.

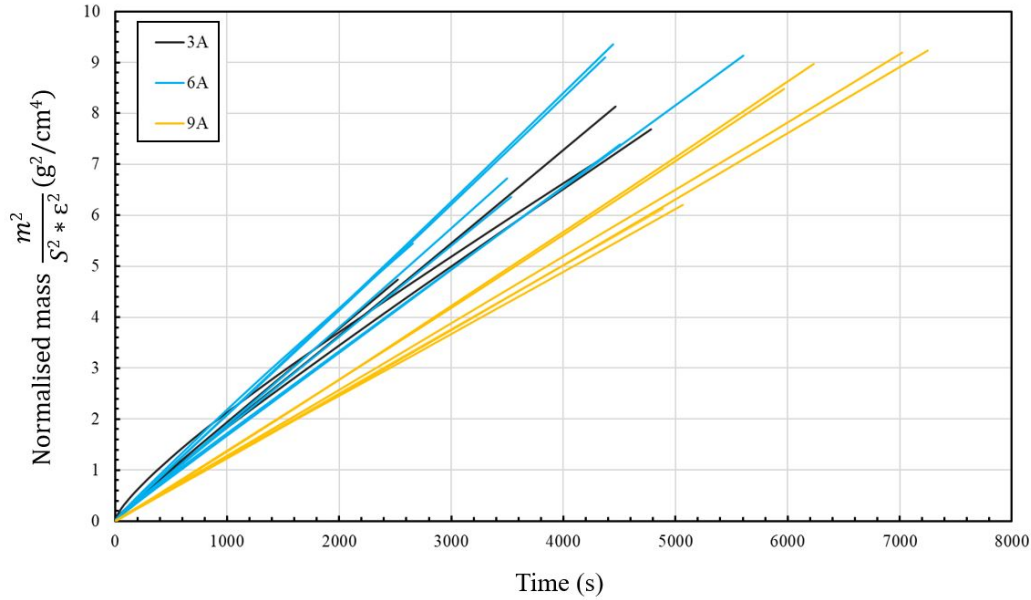


Figure 5.20 Normalised imbibition rates for specimens of varying thicknesses of phase II with n-hexadecane.

The slopes of the square of the impregnated mass of fluid as a function of time exhibit comparable rates for 3A and 6A, but a decrease in rate is observed for 9A specimens. This corresponds to a decrease in the effective diameter for specimen 9A. The d_{50} values for 3A and 6A exhibit a comparable range, whereas the median pore size for 9A is smaller, leading to a reduction in normalized imbibition for the thicker specimens.

The microstructure visualization shows similar pore distribution for the three specimens, as shown in Figure 5.21 based on the relative comparison of porosity associated with the different thickness (3, 6 and 9 mm). There is no noticeable change in the spatial morphology of pore clusters. However, there is a gradual reduction in the effective diameter as the thickness of the matrix increases from 3 to 9 mm. The resulting effective diameter characterizing each pore structure is also given in Figure 5.21.

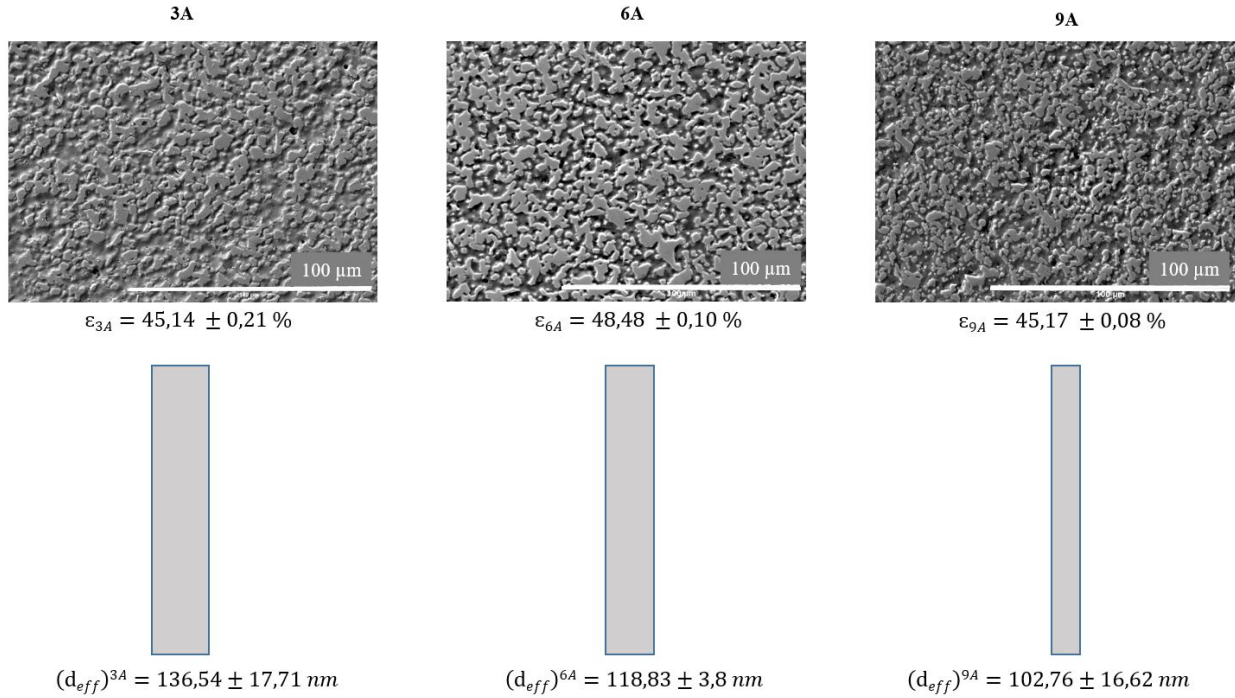


Figure 5.21 Microstructures from SEM observations for specimens 3A, 6A and 9A.

Therefore, it can be said that there will be variation in capillary imbibition for the three specimen types despite having similar porosity. The major change would be attributed to the increasing thickness of the matrix which should have some influence on the pore size distribution through the thickness. We will describe this effect further as a result of the heat treatment that is not perceived equally from the surface of the specimen to its core.

5.2.3 Simulation of capillary imbibition

Through the connectivity of the porous network, the hydraulic conductivity parameter determined by MIP provides valuable information for developing the correlation between the microstructural parameters and the imbibition dynamics. This coupling between the morphology and dynamics of imbibition is facilitated by the Van Genuchten parameter that should be set to simulate the capillary imbibition with FlexPDE. The fitting of the MIP

curves to obtain Van Genuchten parameters n and α for specimens 3A and 9A is shown in Figure 5.22. The corresponding Van Genuchten parameters that are fitted for different thicknesses shows a similar range to depict similar nature of hydraulic conductivity for the specimens produced from the slurry formulation of type A.

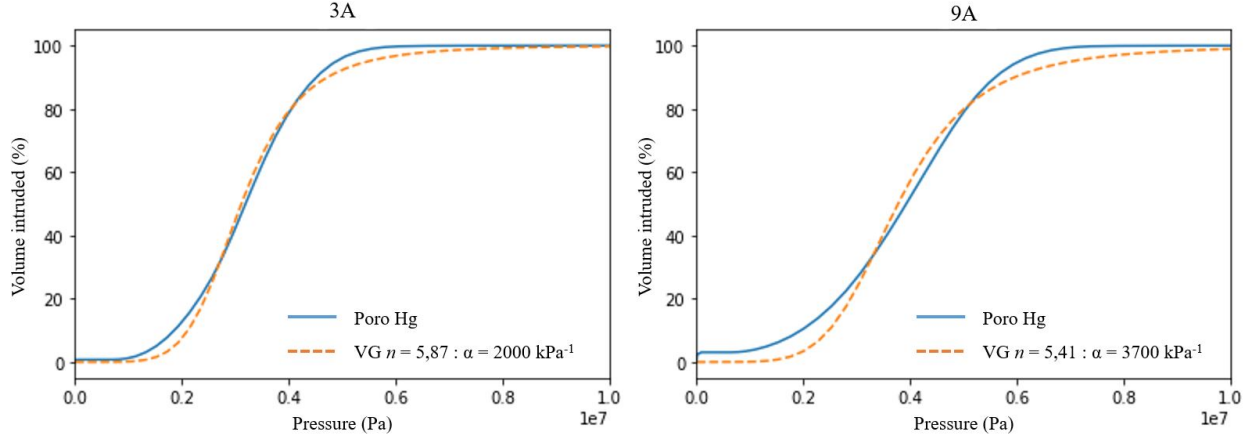


Figure 5.22 Volume introduced as a function of pressure given by MIP with VG function fitting.

The median pore size ranges of 3A and 6A exhibit similarity (Table 5.6), thereby resulting in comparable VG parameters for both thicknesses. However, the variations that arise for an increase in thickness up to 9 mm, combined with the interplay of morphological parameters, can have an impact. From the observation under SEM and MIP experiments, the SiC matrix exhibits a comparable dispersion of pores in its spatial distribution, without any discernible development of specialized pore clusters (Figures 5.17 and 5.21).

A first round of simulation with FlexPDE permits to determine the level of tortuosity to be set in order to fit the experimental curve of normalized mass of impregnated fluid. The fit for specimens 3A and 9A and the resulting values for tortuosity are shown in Figure 5.23. The pore microstructural parameters, the VG parameter n , and the resulting tortuosity τ are given in Table 5.8. Here the simulation is done for a single specimen of 9A; the resulting effective diameter value for 9A is then not necessarily representative of the overall effective diameter for all 9A specimens.

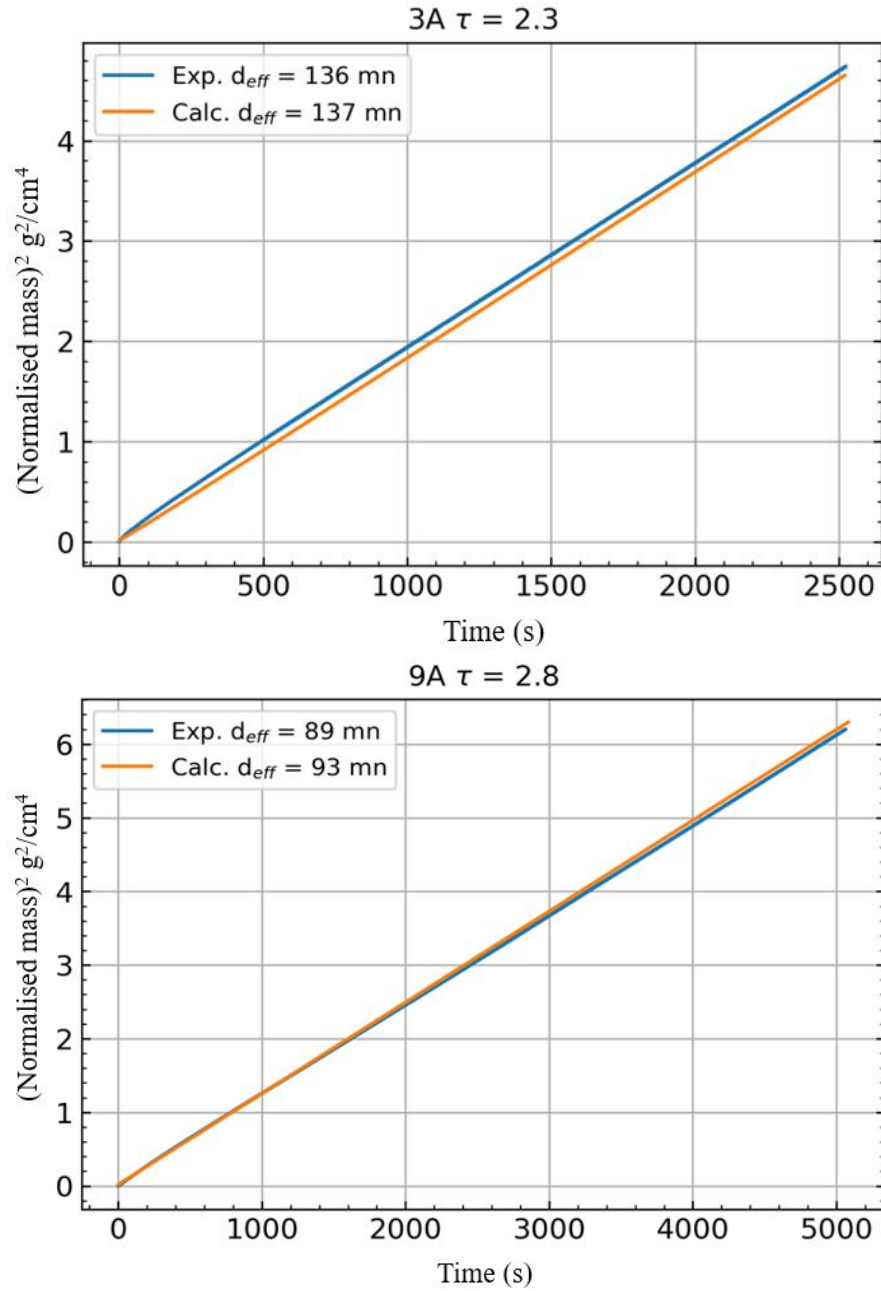


Figure 5.23 Comparison between experiments and simulations of squared normalized mass as a function of time for specimens 3A and 9A. The tortuosity τ is adjusted to fit the experimental data.

Specimen	ε [Twe] (%)	d_{eff} (nm)	d_{50} [MIP] (nm)	VG n	τ (-)
3A	45.14	136.54 ± 17.71	390	5.87	2.3
6A	48.48	118.83 ± 3.80	409	4.52	2.8
9A	45.17	102.76 ± 16.62	321	5.41	2.8

Table 5.8 Microstructural parameters used in Richards' approach with effective diameter estimated using Washburn law.

Similarly to what was observed in phase I, the existence of a saturation gradient is likely contingent upon certain morphological parameters, including but not limited to porosity (ε), median pore size (d_{50}), and tortuosity (τ).

Figure 5.24 illustrates the identification of saturation level with FlexPDE that matches the detection of the flow front height at the surface of specimens 3A and 9A during capillary imbibition. Some efforts were deployed to identify the parameter that has a greater influence on the saturation gradient in the longitudinal direction and to establish its impact in order to advance the understanding of the dynamics of complex shapes with similar and different formulations.

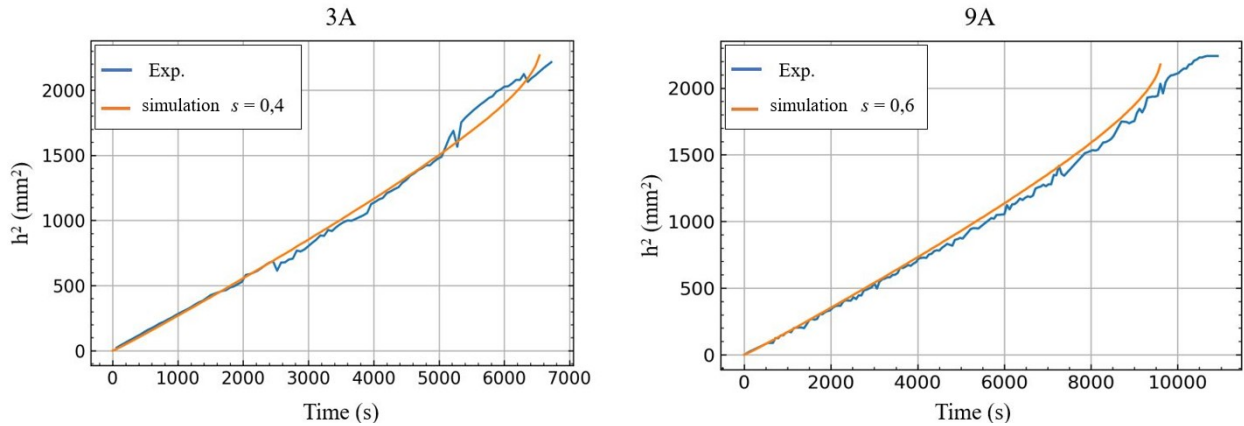


Figure 5.24 Comparison between experiments and simulations of the evolution of imregnated liquid height h as a function of time for specimens 3A and 9A.

From the results of phase I based on the observation of 3D images from CT scans of interrupted tests, it was clear that the fluid flow front was not flat (Figure 5.14). The parabolic flow front is characterized by faster imbibition along the central axis of the specimens. This feature was not taken into account in the numerical simulation of capillary imbibition in phase I.

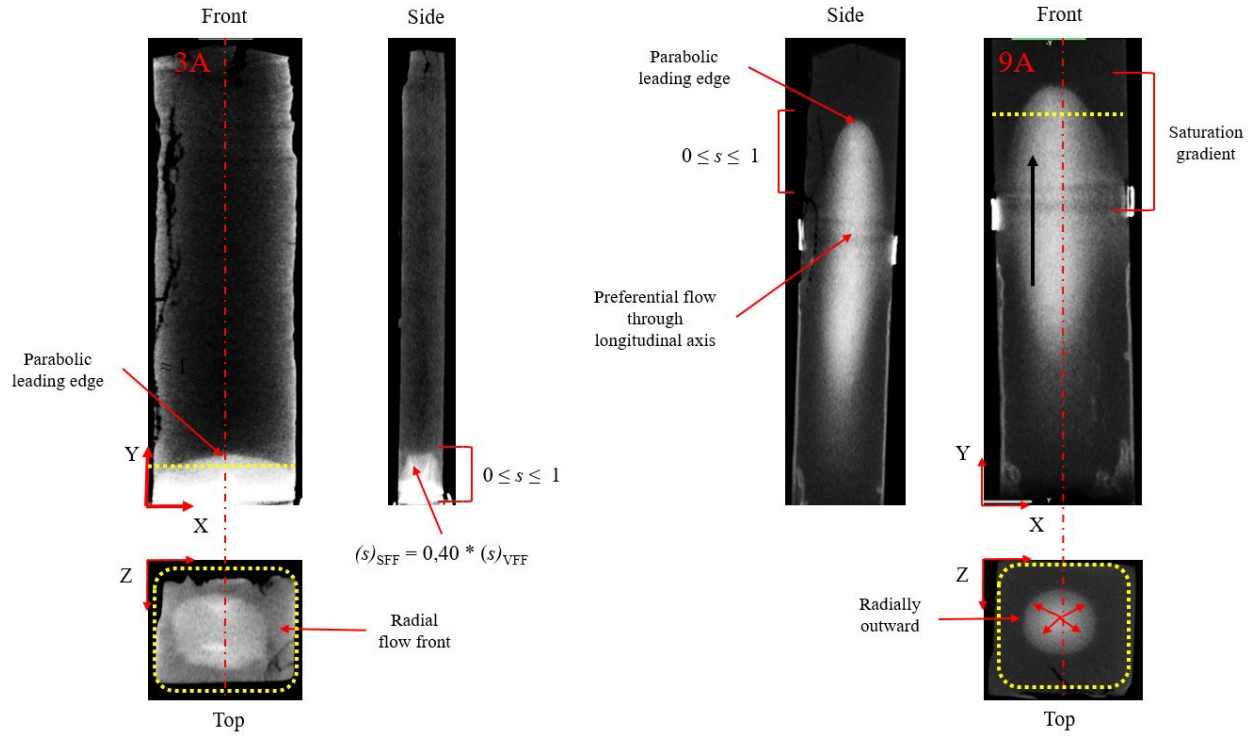


Figure 5.25 Three-dimensional flow visualization by micro-tomography after interrupted capillary test with *exo*-DCPD. Left: specimen 3A. Right: specimen 9A.

The observation of the same phenomenon on specimens of phase II reveals that the parabolic flow front is enhanced when the thickness of the specimen increases (Figure 5.25). For thinner specimens (3A), the flow front is almost flat. A second round of capillary flow simulation with FlexPDE was then carried out to identify the causes of this phenomenon.

5.2.4 Relation between the thickness and the pore network characteristics

In phase II, it is possible to obtain a parabolic flow front with faster imbibition kinetics along the center line of the specimen by introducing a median pore size gradient that is imposed on the corresponding microstructure in an arbitrary manner. It validates the effect of heat treatment on the different zones of the matrix namely surface and center. This approach highlights the significance of median pore size in exerting control over the imbibition rate.

The variation of the median pore size across the thickness maybe attributed to the microstructural response of the material during high-temperature heat treatment. The effect of heat treatment could be more pronounced near the surface of the specimen, leading to a more extensive consolidation of the granular microstructure.

For typical SiC granular materials, it is well known from our industrial partner that all of

the porosity on the consolidated matrix is open prior to THT (no closed porosity). THT causes bridging between grains, which increases the mechanical strength of consolidated SiC and rearranges the porosity in the presence of larger pore sizes d_{50} . Then for the simulation, a methodology was followed involving the utilization of a parabolic gradient (second-order polynomial) to be set to take into account the variance in median pore size between the surface and center, as opposed to relying on a single value for d_{50} .

The parabolic flow front generated by distinct microstructures could be influenced by the median pore size exhibiting a larger value at the surface and a smaller value on the interior. In order to approach the typical parabolic front that was observed experimentally, a parabolic reduction of the d_{50} of 12-16 % (see Table 5.9) was imposed between the surface and the center of specimens 6A and 9A. The resulting saturation profiles are illustrated in Figure 5.26.

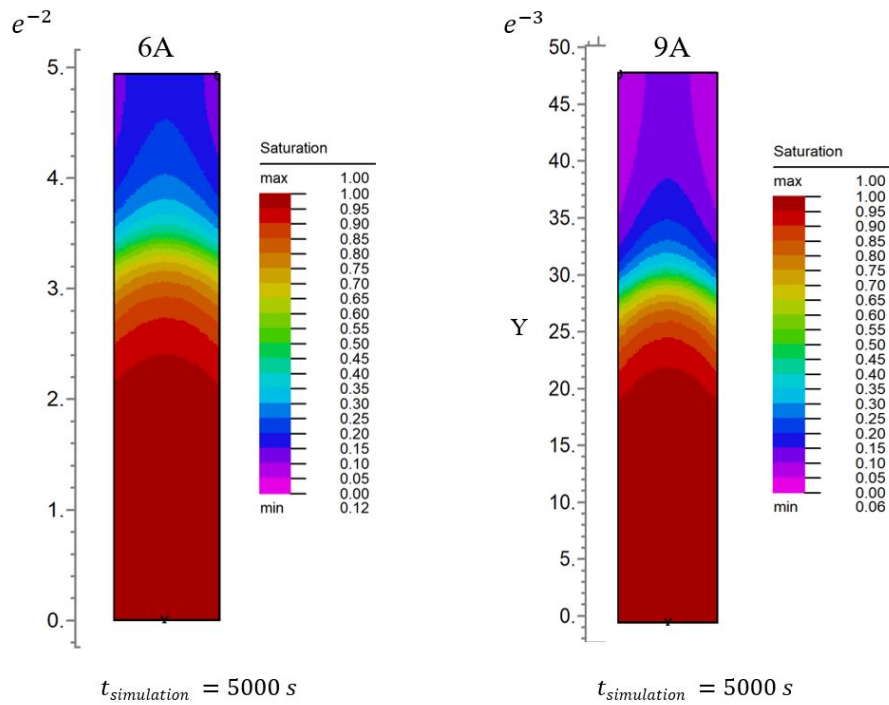


Figure 5.26 Saturation profiles predicted by numerical simulation with FlexPDE at $t = 5000$ s for specimens 6A and 9A.

Specimen	Center	d_{50} (nm)		ε (%)	VG n	τ (-)
		Surface	Change (%)			
6A	359	409	- 12	48.48	4.52	2.8
9A	271	321	- 16	45.17	5.41	2.8

Table 5.9 Parameters used in the FlexPDE simulations for specimens 6A and 9A of phase II.

With the aim of confirming this effect of heat treatment on the gradient of microstructure, some specific tests were carried out to highlight the causes of the parabolic profile of the flow front. The first cause that could explain the slower imbibition kinetics near the surface of the specimens is a boundary effect. For some unclear conditions, the surface could retard the progression of fluid close to the surface. To verify this hypothesis, a heat-treated specimen was cut along its center line to observe the line of flow front on the newly created surface, as shown in Figure 5.27.

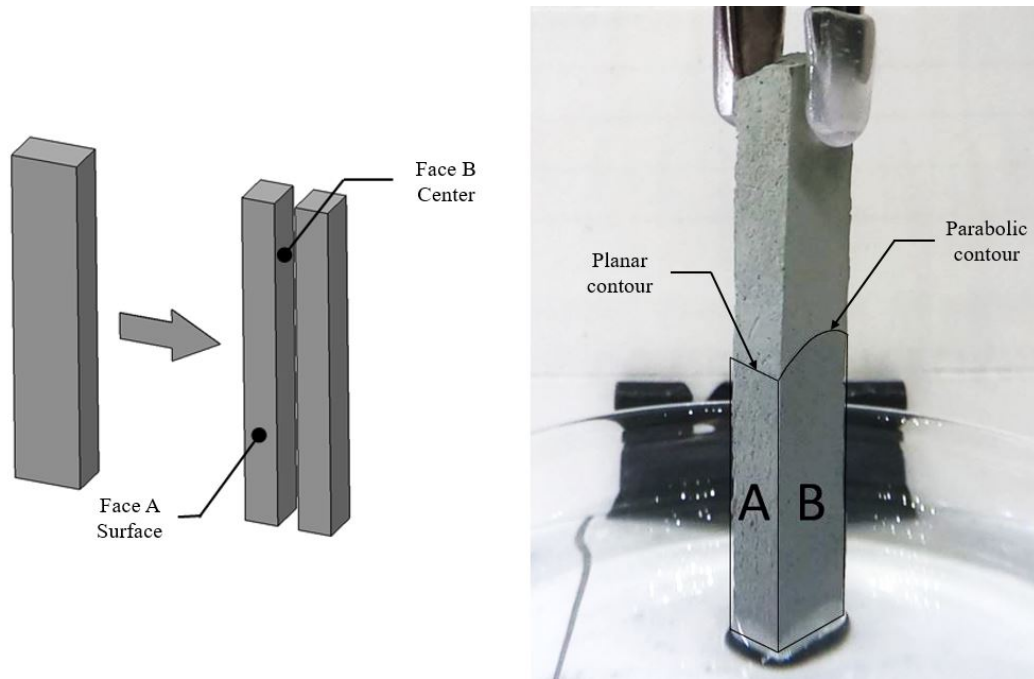


Figure 5.27 Different surface flow front contour observed on the original surface (Face A) and the newly cut surface (Face B).

On the original specimen surface (Face A), the parabolic profile is not observed; only a straight line characterizes the flow front on the four faces of the specimen. However, on the cut surface passing through the center line of the specimen (Face B), it was now possible to observe the parabolic contour of the flow front. This means that the newly cut surface did

not act to slow down the fluid progression. So the hypothesis of the surface retardation effect should be rejected.

Another test was carried out to verify the hypothesis of the effect of heat treatment. A specimen of type 9A was produced to be tested for capillary rise experiment *before* heat treatment. The results shown in Figure 5.28 from tomography imaging are very clear: the fluid flow front is not parabolic but flat. This is a clear demonstration of the validity of the hypothesis of the effect of heat treatment on the evolution of microstructure. Even if this effect cannot be clearly characterized by SEM images, nor by median pore size measurement by MIP on samples extracted from the center and at the surface, the sensitivity of interrupted capillarity imbibition with *exo*-DCPD proves to be better.

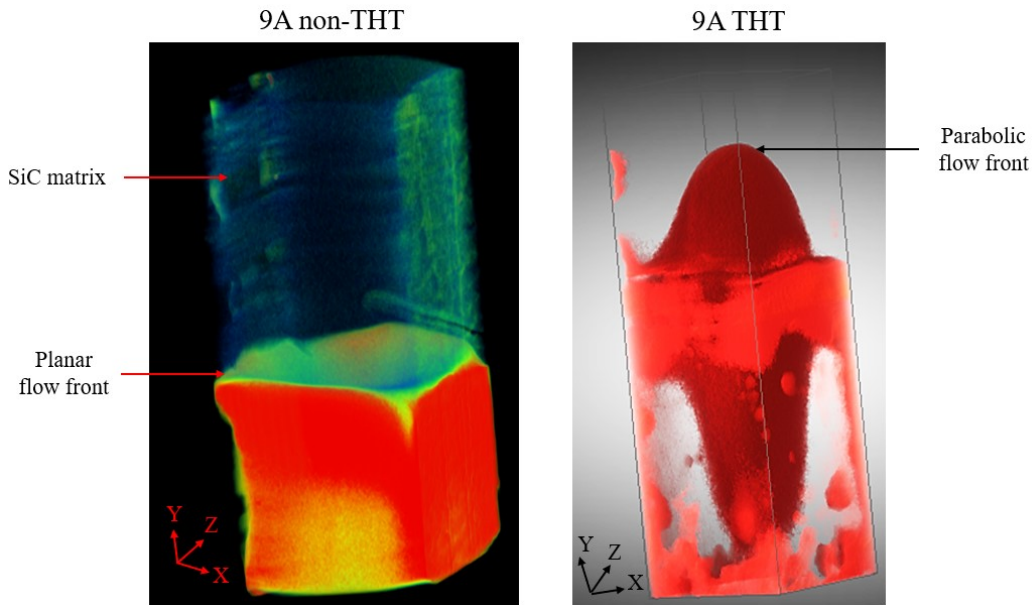


Figure 5.28 Observation by micro-tomography after interrupted capillary tests of the formation of volume flow front through SiC 9A specimens before and after heat treatment (THT). The color scheme does not seem to indicate analysis on similar specimen.

5.2.5 Concluding remarks for phase II

The intention of phase II experiments was to verify the effect of the thickness of specimens on the kinetics of capillary imbibition. By using the same slurry formulation (type A) for three thicknesses (3, 6 and 9 mm), it was expected to obtain the same pore microstructure in all specimens. Results showed that it was not the case.

The observed 3D parabolic profile for the flow front by micro-tomography indicated that a slight reduction in the median pore size d_{50} from the surface to the center of the specimen

could lead to this parabolic profile. The gradient of microstructure seems to come from the heat treatment for the consolidation of specimens that has different effects through their thickness. Even if the pore size variation is too small to be characterized by SEM images or local MIP characterization, the simulation of the capillary imbibition with FlexPDE shows good agreement with the experimental results.

There should be a threshold in the thickness of the specimens under which the heat treatment brings no significant gradient in the microstructure of granular materials. For the context of our study, this should be around 3 mm where the experiments show an almost flat flow front. For thicker specimens, the granular material at the surface sees higher temperature during heat treatment, causing the opening of pore channels resulting in a slight increase of d_{50} .

This could explain why the tortuosity for specimen 3A is lower than that of specimens 6A and 9A (Table 5.8); the overall pore size is larger and the pore structure offers less resistance to fluid flow. For specimens 6A and 9A, the tortuosity is characterized by averaging its value over the whole volume of the specimen. The weight of the surface value could be much smaller than that of the core for the thick specimens.

In the case of graded pore size across the thickness, it is true that the capillary kinetics is faster along the center line, but there should also be radial flow along the pore size gradient. In this case, it corresponds to capillary flow in heterogeneous materials and this will be the subject of phases III and IV.

5.3 Impact of complex geometry and heterogeneity: phase III

The aim in the definition of this phase III is to better understand the behavior of the wetting fluid flow in channels of complex shapes with diverging or converging section area that are typical of those in real SiC/SiC composites during the step of melt infiltration with liquid silicon. The typical microstructure of such a ceramic composite was shown in Figure 2.12.

In this case, the wetting liquid has to travel in channels of granular SiC matrix between fiber tows that are not permeable to the liquid phase due to the protective CVI layer that has the effect to close the intra-tow porosity. The capillary flow really occurs through the fine porosity between particles of the granular matrix. The channel size is at a much larger scale than the pore size between particles.

However, at this scale, for example in diverging section area channel, it could be possible to envisage incomplete filling of the porous channel by the liquid since it has to enter the large section area through a smaller section area which limits the flow rate. In this case, an undesirable unfilled (or dry) matrix region would result. Another phenomenon that occurs

in real CMC matrix is the heterogeneous pore network characteristics from one point to the other. It would then result in capillary pressure gradients that could influence the behavior of capillary flow in the granular matrix.

During the course of this experimental phase, a lot of specimen geometries were tested proving that it was not easy to fabricate specimens with a varying channel section area ratio of 1:10 as targeted initially. Also, the brittleness of the granular material before heat treatment impedes the fabrication of specimens in the size scale of 100 μm . Finally, there was also a practical limitations coming from the equipment dedicated to heat treatment and capillary rise experiments.

The incorporation of P shape specimens possessing intricate geometrical features, encompassing diverging and converging channel section area and heterogeneous compositions comprising two distinct formulations has been designed in phase III. The morphology of these P shape specimens presented earlier is reproduced here in Figure 5.29. In this study, the nominal thickness of the specimens for the current phase remains constant at 6 mm.

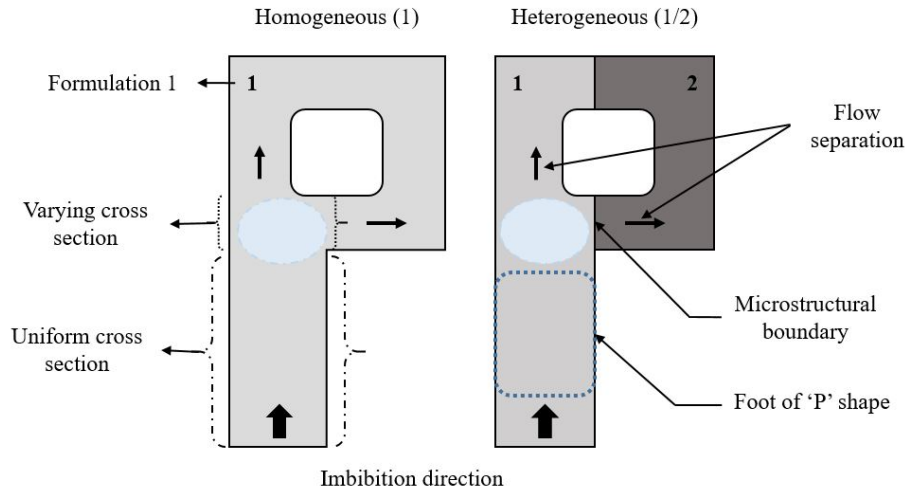


Figure 5.29 Configurations of the two types of specimen for phase III with homogeneous and heterogeneous formulations with complex P shape geometry.

5.3.1 Homogeneous P shape specimens

The objective of this first part is to characterize the imbibition dynamics observed in a homogeneous porous material having complex contour geometry. As shown in Figure 5.29, the liquid capillary flow is introduced in the specimen from the lower section of the foot of the P shape specimen. When the flow front arrives in the zone where the cross section of the specimen increases (at the bottom of the square loop of the P), it is possible to observe the

behavior of the capillary flow in diverging section area. The continuous flow is then separated into two branches with reduced section area (converging flow).

Characterization of homogeneous P shape specimens

In order to properly characterize the microstructure and pore network of each formulation, the mold cavity was modified to permit the production of two P shape homogeneous specimens and two rectangular bars that were used to verify the homogeneity of the microstructure within a single slurry cast batch. For the specimens of the first part of phase III, the following designation was used to differentiate the three slurry formulations: P(A), P(B) and P(C).

To determine the median pore size d_{50} of each specimen formulation by mercury intrusion porosimetry (MIP), a small sample was extracted from the leg of the P shape specimens. This permits also to evaluate the level of porosity in the specimens. The MIP curves from the three types of specimens are shown in Figure 5.30.

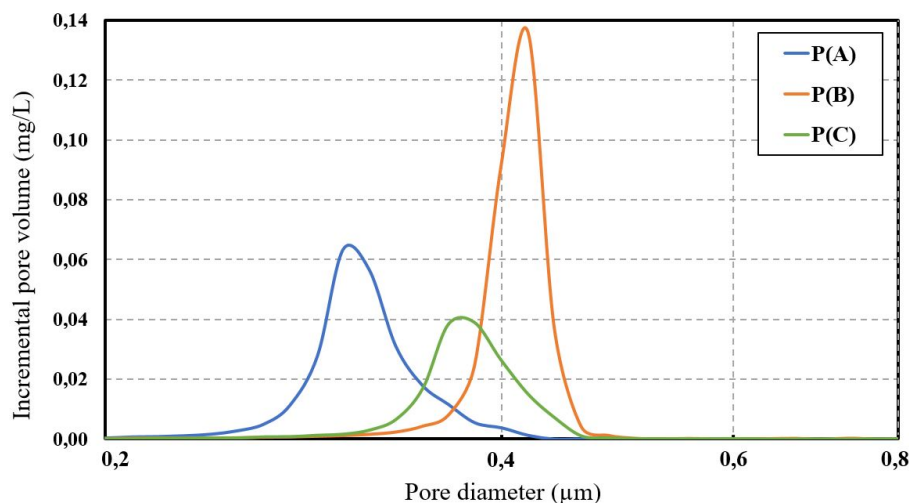


Figure 5.30 Pore size distribution with the incremental pore volume for P shape geometry of the three formulations.

For the characterization of porosity, as mentioned before, since the specimens have homogeneous pore structure, the measure coming from triple weighing (buoyancy method) was preferred because it gives a global value for the whole specimens. The pore characteristics values are given in Table 5.10.

If we compare these experimental results with those obtained for the three slurry formulations tested in phase I (Table 5.2), we observe that in terms of the porosity, the three formulations rank in the same decreasing order: $B > A > C$. It is slightly different for the value of d_{50} . If the smallest value is obtained in both phases for type A formulation (the more compacted),

Specimen	ε [Twe] (%)	ε [MIP] (%)	d_{50} [MIP] (nm)	Thickness (mm)
P(A)	43.30 ± 0.26	44.23	318	5.97 ± 0.12
P(B)	49.63 ± 0.02	51.35	422	6.10 ± 0.09
P(C)	35.23 ± 0.38	35.73	388	5.20 ± 0.67

Table 5.10 Microstructural parameters for the three homogeneous formulations with P shape geometry.

the order is reversed for types B and C where d_{50} is larger for type C in phase I and for type B in phase III. As described in the previous phases, the combination of porosity, median pore size and tortuosity values conditions the kinetics of capillary rise.

Capillary rise experiments in homogeneous specimens

For each slurry type formulation, two P shape specimens were produced per slurry cast batch. The capillary rise experiments were carried out with hexadecane at room temperature on these P shape specimens by bringing into contact the foot of the P with the surface of hexadecane bath. The kinetic of capillary rise experiments is illustrated in Figure 5.31 where the square of the impregnated fluid mass (corrected by subtracting the effect of the meniscus) is plotted as a function of time.

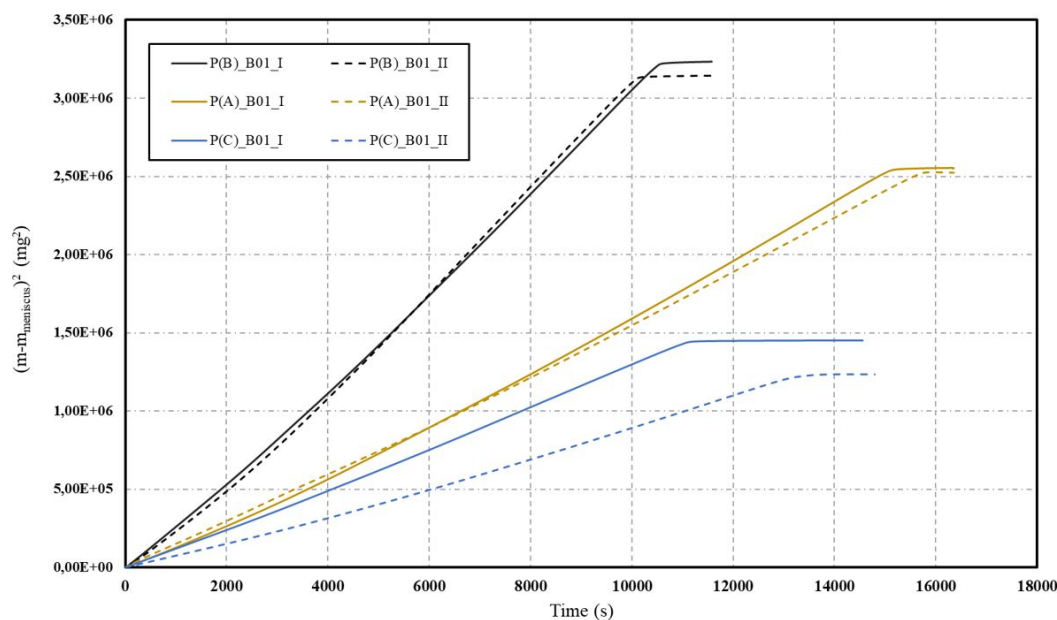


Figure 5.31 Capillary imbibition rise kinetics for the three formulation types of homogeneous P shape specimens. The mass of impregnated fluid in the specimens is corrected by taking into account the effect of the meniscus.

As expected, the diffusive $m^2(t)$ law is almost characterized by straight lines on m^2 versus t graph. A slight change of slope (increase) occurs between 4000 and 6000 s where the flow front enters the diverging section area zone. This graph shows that porous microstructure of types A and B specimens is highly reproducible since the respective two curves for each type produced in the same batch (B01) are almost superposed.

The situation is different for type C where, in the same slurry cast batch, the curves characterizing the capillary kinetics are significantly different. This could be explained by the inherent difficulty of producing type C specimens by slurry casting due to longer drying time and specimen handling during demolding. However, the ranking of capillary rise kinetics (slope of the straight lines) is the same as the one obtained in phase I. In decreasing order of capillary kinetics, we have B, A and C.

When looking at the detection of flow front from the surface of specimens during capillary imbibition experiments, it is possible to characterize the progression of the fluid when it goes through the diverging section area towards the separation in the two branches of the P loop. This is illustrated in Figure 5.32 where the flow front line in the two branches is highlighted by red lines. These images were obtained for the same total capillary impregnation time of 6000 s. As expected, since the kinetics of impregnation is faster for type B specimen, the flow front progressed further in the specimen.

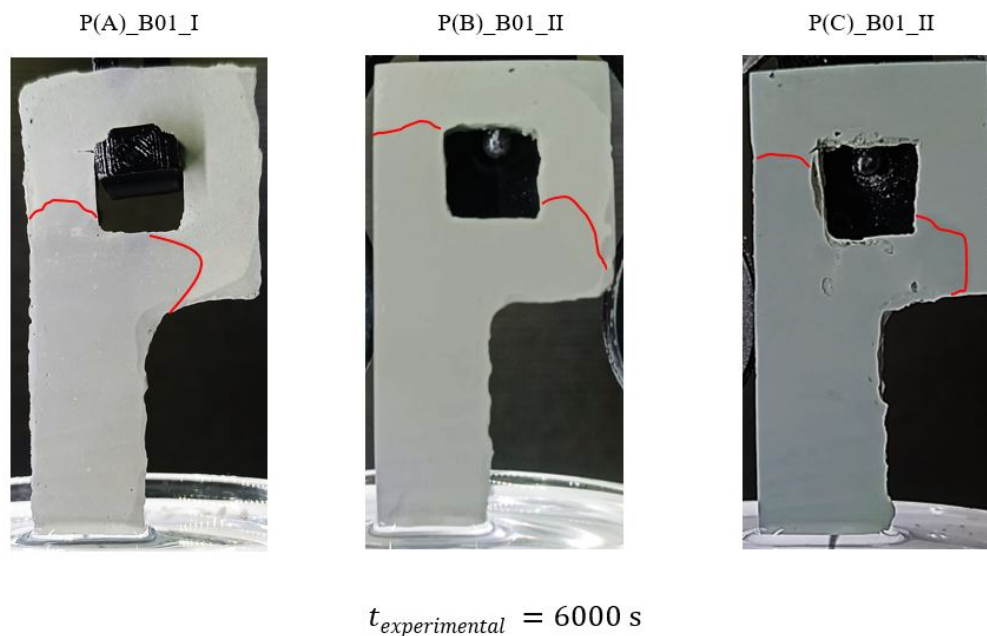


Figure 5.32 Level of hexadecane observed at the surface of specimens as diffuse flow front progresses in the diverging section area zone in the P shape specimens of type A, B and C. The three images are given for the same imbibition time of 6000 seconds.

When the liquid flow front attains the zone where the section area increases (at the top of P leg), the flow front *velocity* certainly reduces. However, since the pore structure is homogeneous through the whole specimen geometry, the capillary pressure is the same everywhere, meaning that the fluid *flow rate* should be about the same because it is limited by the section area of the P leg. This is the reason why the capillary kinetics curves $m^2(t)$ shown in Figure 5.31 do not show a significant change of slope that would be indicative of the change in pore structure.

The observation of volumetric fluid flow in 3D by tomography after capillary rise experiments with *exo*-DCPD is illustrated in Figure 5.33. The fluid flow profile observed in 3D is well correlated with that observed in 2D from the surface flow front.

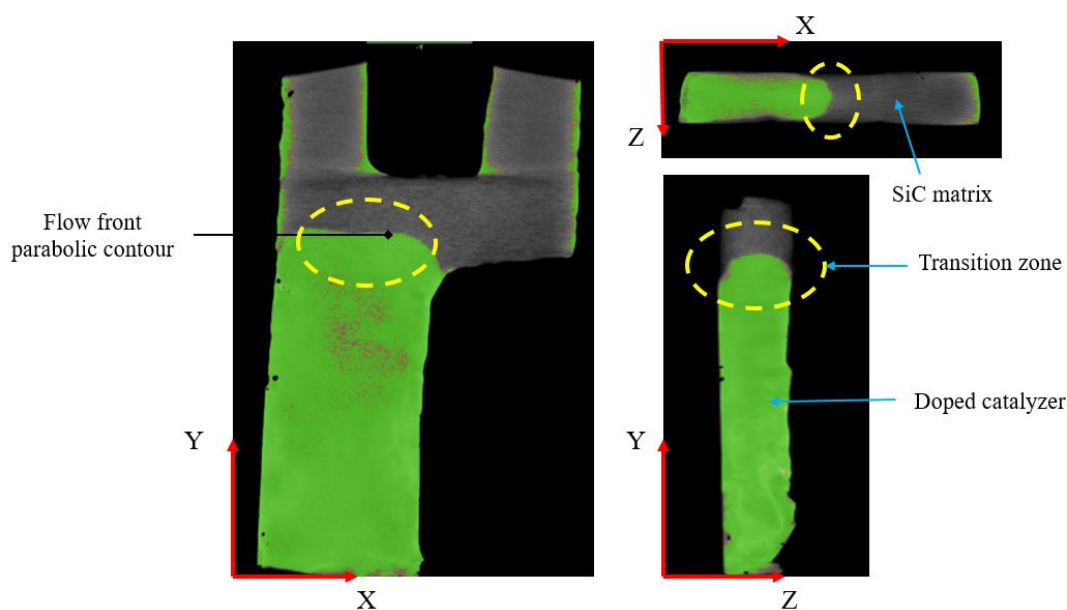


Figure 5.33 Evolution of the volumetric flow front shows a parabolic contour that is visible from all orthographic views for C type formulation of P shape specimen of ≈ 6 mm thickness. The imbibition takes 3500 s for the specimen shown.

The flow front within the SiC matrix exhibits distinct progression along two edges, each representing distinct morphological characteristics. When the fluid front reaches the transition zone, the process of imbibition occurs as a result of the divergent cross section and separation. The presence of a parabolic front can be observed in the XZ and YZ planes. The macroscopic contact angle with the contour of the P shape geometry undergoes variation as the diffuse fluid front progresses and forms a leading edge along the axis of imbibition for different cross-sectional areas.

The flow restriction along the edges leads to the development of viscous dissipation, which

in turn causes a variation in the imbibition length. This variation is observed as the diffuse front followed by the inertial front, with a more uniform surface front boundary. The contour of the flow front aligns with the observation that has been examined in Figure 2.27, which illustrates a comparable impact of the fluctuating contact angle resulting from alterations in boundary characteristics. The development of a smaller contact angle serves to impede the advancement of imbibition, leading to a discernible disparity in progression as the fluid surpasses the transition zone.

Capillary rise simulation in homogeneous specimens

The numerical simulation of capillary flow in P shape specimens was carried out with FlexPDE by using the properties of hexadecane given in Table 4.4 and the pore structure properties of type A formulation given in Table 5.10. The Van Genuchten parameter n and the tortuosity were the same than those used in phase I for specimens 6A. The result of simulation is illustrated in Figure 5.34 where the saturation profile is shown for various simulated times.

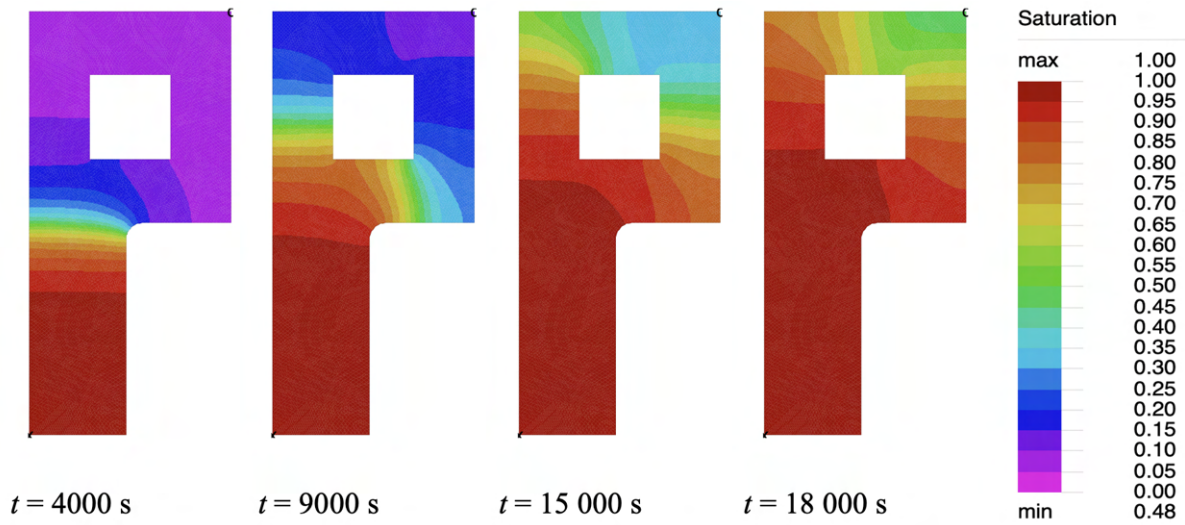


Figure 5.34 Saturation profiles for capillary flow of hexadecane in homogeneous P shape specimen of type A. Saturation contours for 4000, 9000, 15 000 and 18 000 s simulated time.

The simulation shows that when the flow front arrives at the diverging zone, where the section area increases, the flow front adopts a curved shape to enter the two branches of the P loop. As shown in Figure 4.33 that illustrates simultaneously the definition of the meshing and the saturation profile, it appears that FlexPDE refines automatically the meshing around the position of the front flow that corresponds to the green color in the saturation contour graph, which is for a saturation of about 50 %.

This is also similar to what we obtained in phase I when we tried to correlate the level of simulated saturation with the position of the flow front that was observed on the surface of the specimen. If we consider now that the observable flow front at the surface corresponds to the position of $s = 0.5$ as shown in Figure 5.34, we see that the flow front arrives at the top of the P leg after about 4000 s. After about 9000 s, the flow is well developed in the two branches of the P loop.

The two flow fronts should meet in the upper right corner of the P loop after about 15 000 to 18 000 s. If we compare the experimental curve of $m^2(t)$ given in Figure 5.31 with that resulting from simulation (Figure 5.35), we note an acceptable correlation to determine the end of the filling after 15 000 s, considering the variation in the thickness of the specimen that could vary locally to influence the evaluation of the volume of impregnated liquid and its mass. Similar qualitative results have been obtained after simulating the behavior of capillary flow in P shape specimens of types B and C.

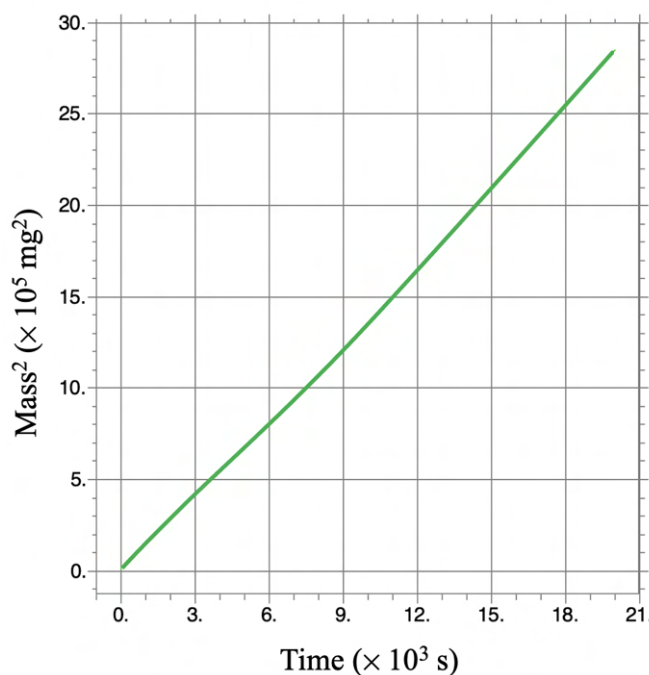


Figure 5.35 Simulated capillary imbibition rise kinetics for homogeneous P shape specimens of type A.

The numerically simulated curve for the kinetics of capillary flow (Figure 5.35) shows a slight break in the straight line between 6000 and 9000 s, as it was observed also in the experiments with P shape specimens (Figure 5.31). The increase in capillary kinetics could be attributed to the smaller relative friction effect of the edges of the specimen due to the enlarged section area of the flow front. It is finally important to mention that even if the design of the P

shape specimen led to the occurrence of diverging and converging flows in different locations, the ratios of flow section areas were not large enough to create dry zones in larger section areas. It was verified experimentally and by simulation that all the volume of pores in the material becomes at a certain point filled by wetting fluid.

5.3.2 Heterogeneous P shape specimens

For the second part of phase III, the heterogeneous configuration combines the geometrical P shape complexity with the transition zone generated at the interface between the two pore network formulations. The methodology to fabricate the specimens was described in Section 4.2.2 and illustrated in Figure 4.14.

In a single batch of slurry cast, it was possible to produce two P shape specimens with heterogeneous microstructure and two reference bars. For example, in the combination of types A and B slurry formulations, we obtained specimens P(AB) and P(BA). The P(AB) designation denotes that the formulation of type A is located on the foot section (bigger volume) of the P where the fluid enters the specimen, while the formulation of type B is located on the other half side of the loop of the P that complements the A formulation.

In addition to the complexity of the shape causing diverging and converging flows, the heterogeneous P shape specimens permit to observe the behavior of capillary flow when it crosses an interface (between the two formulations) that is perpendicular to the direction of flow in the two branches. The interface combines with the changing cross section for the P shape specimen that changes the macro imbibition dynamics (converging and diverging flows) of the infiltration.

Due to the inherent difficulty in the production and handling of the heterogeneous P shape specimens, the presence of macro-cracks in and around the interface has been observed, as shown in Figure 5.36. This would have an impact on the imbibition dynamics, potentially leading to dispersion in the results of capillary kinetics from one specimen to another. The alteration would inevitably impact the spatial distribution of the fluid phase that displaces the air from the porous network and subsequently occupies the empty spaces. The formation of adjacent columns occurs when the fluid that has been absorbed is separated at the transition zone and proceeds through the interface, where there is a change in the microstructure.

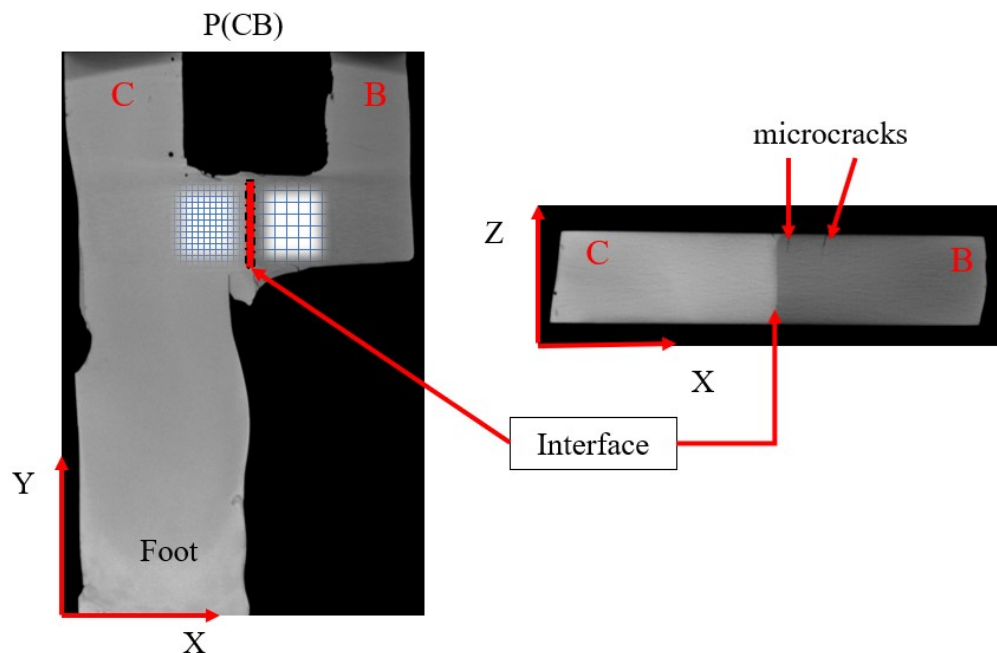


Figure 5.36 Typical X-ray tomography of a P shape specimen with uniform thickness and two different formulations. Image on the right shows small microcracks initiated from the surface of the specimen.

Characterization of heterogeneous P shape specimens

The microstructural and poral network characterization of the heterogeneous P shape specimens involves the extraction of three samples at different locations. The schematic for the identification of relevant zones has been shown in Figure 5.37. For example, when a sample is designated as P(AB), it means that it has been extracted around the interface separating the two granular formulations. For sample designated as P(AB)/A, it means that it was extracted on the type A side of P(AB) specimen, and similarly for specimen designated as P(AB)/B.

After the extraction process, the specimen undergoes a comprehensive oven-drying procedure before MIP to effectively eliminate any moisture present within its porous structure. This meticulous drying process aims to provide a more precise assessment of their porosity.

The characterization of the microstructures of the three sub-classes of samples obtained from specific zones reveals the presence of microstructural diversity within a single heterogeneous specimen. These results are illustrated in Figure 5.38 showing the pore size distributions resulting from MIP experiments for three combinations of heterogeneous P shape specimens.

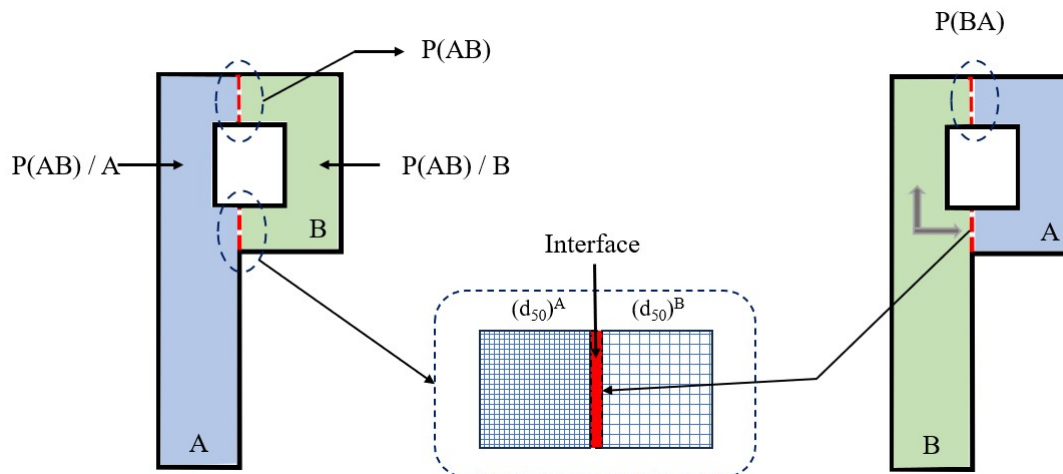


Figure 5.37 Schematic indicating the locations for the extraction of sub-samples from the P shape specimen, with the depiction of the morphology on both sides of the interface.

The AB and BC specimens exhibit a distinct manifestation of the alteration in median pore size, which is evident through the presence of two peaks representing the two distinct median pore sizes within the sample located at the interface. For AC types of specimens, the distinction between the two peaks in $P(AC)$ sample is less clear. However, taken separately in samples $P(AC)/A$ and $P(AC)/C$, the two regions show clear difference in d_{50} .

In addition to MIP experiments that characterize locally the pore network (porosity and median pore size) in different specimens, the overall porosity was also measured by triple weighing, while taking into account that the resulting value of porosity is averaging the porosity level of both formulations in heterogeneous specimens. The parameters obtained in details have been organized in Table 5.11 for the purpose of facilitating comparison between various configurations of the P heterogeneous specimens.

From the results summarized in Table 5.11, some details can be pointed out to help the interpretation of capillary imbibition experiments that will be presented in the following section. For specimens AB, the value of porosity evaluated by MIP is abnormally lower for B side compared to A side. However, the averaged porosity evaluated by triple weighing gives value slightly higher for specimen $P(BA)$ than that of specimen $P(AB)$, which is expected since the proportion of B type formulation is larger in the first case, influencing then more importantly the average porosity. For specimens BC, the trend in porosity values goes in the same way as what was obtained in phase I. However, the MIP porosity of C type formulation is abnormally low. The trend for the porosity of AC specimens is also similar to what was observed in phase I. In terms of d_{50} , the ranking of values for the different formulations

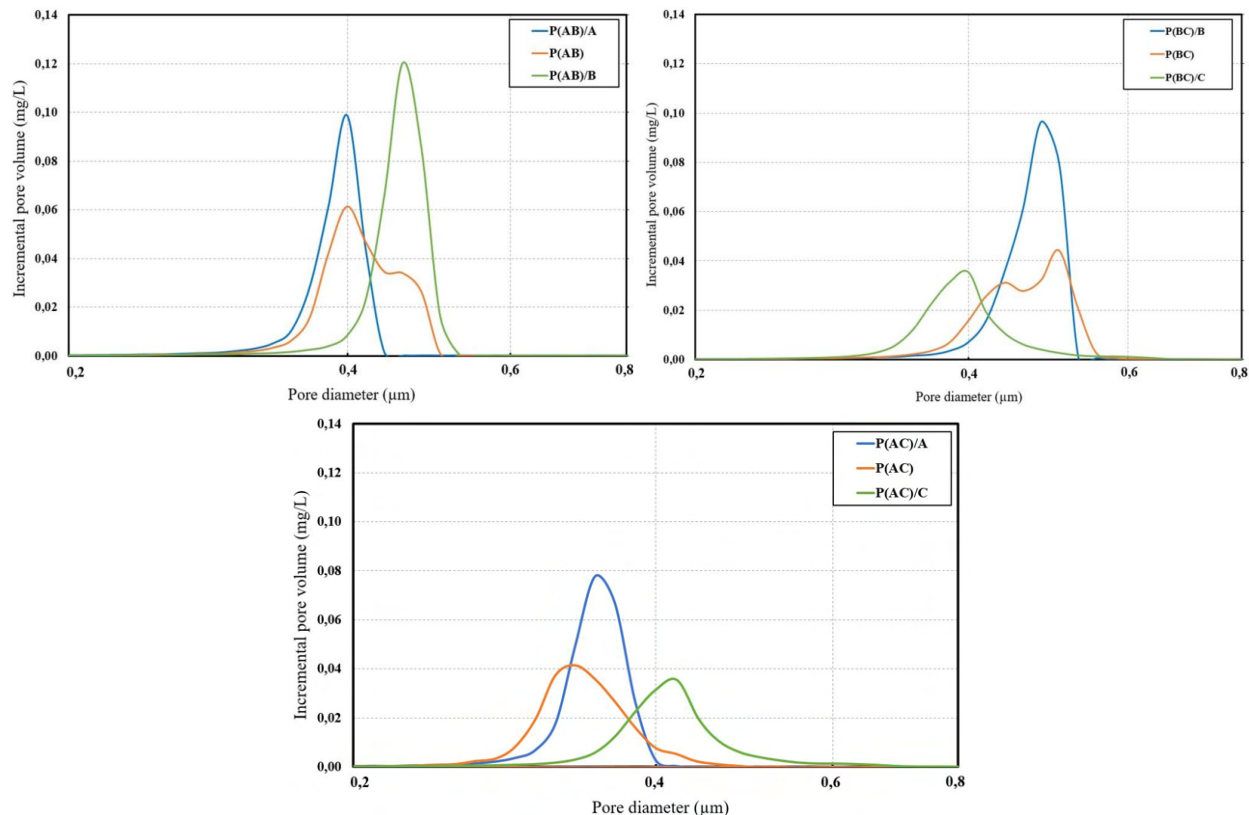


Figure 5.38 MIP characterization of heterogeneous P specimens with variations from one location to the other.

Specimen	ε [Twe] (%)	ε [MIP] (%)	d_{50} (nm)
P(AB)	47.64 ± 2.53	46.24	361
P(AB)/A	—	47.70	349
P(AB)/B	—	45.25	387
P(BA)	49.10 ± 1.94	—	—
P(CB)	40.21	24.36	419
P(CB)/B	—	50.32	444
P(CB)/C	—	21.76	395
P(CB)	40.08	—	—
P(AC)	39.10 ± 5.38	40.60	346
P(AC)/A	—	47.36	358
P(AC)/C	—	35.23	339
P(CA)	39.82 ± 1.09	—	—

Table 5.11 Comparison of porosity and median pore size between the three combinations of heterogeneous P shape specimens.

respects the trend obtained in phase I, except for AC specimens where the ranking of median pore size between formulations A and C is reversed.

From all these observations, two remarks should be considered in the interpretation of capillary imbibition experiments on heterogeneous P shape specimens:

- Due to the difficulty in reproducing exactly the same granular media formulation of each type, a significant dispersion in pore network characteristics is observed, especially when they are measured locally through MIP method.
- The resulting capillary imbibition kinetics for heterogeneous P shape specimens cannot be compared to those that were obtained in phase I.

Capillary rise experiments in heterogeneous specimens

The goal of the capillary imbibition experiments is to verify if it is possible to observe the combined effect of the morphology of the specimen and its microstructure on the progression of imbibed fluid. The two zones that are formed by the joining of the two different formulations would exhibit different imbibition characteristics that would further provide the fundamental basis of the capillary forces at play.

The capillary imbibition as observed in heterogeneous AB configurations exhibits a notable disparity between the larger sections composed of two distinct types and the smaller sections that are interconnected via an interface layer as seen from Figure 5.39. The evolution of capillary flow kinetics with time ($m^2(t)$) is also given for both P(AB) and P(BA) configurations, with two distinct specimens for each configuration.

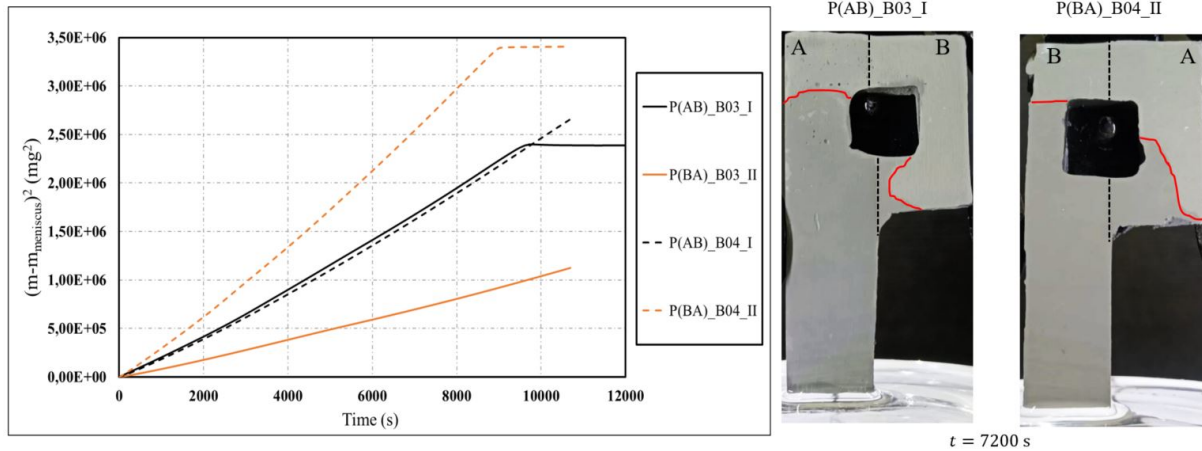


Figure 5.39 a) Progression of capillary imbibition with time for heterogeneous P shape specimens of type AB. b) Images of surface flow front (diffuse) between the two heterogeneous configurations of A and B type microstructure after 7200 s.

For all the four specimens tested, the hexadecane capillary imbibition was carried out until the specimens were completely filled. This occurred after about 9000–10 000 s. Even if the two

P(AB) specimens were fabricated in different batches (B03 and B04), the imbibition kinetics were very similar. This was not the case for P(BA) specimens, where in one case the kinetic was slower than P(AB) and in the other case faster than P(AB) specimens. Apart from the dispersion in the preparation and casting of the slurries, Figure 5.39-b reveals that the overall geometry of the specimens can vary a lot from one batch to the other, bringing significant dispersion in the measure of imbibed fluid mass through the experiments. Nevertheless, the $m^2(t)$ curves for heterogeneous specimens show a similar trend to those resulting from capillary imbibition of homogeneous P shape specimens. A small increase in the slope of the curves around 4000 s corresponds to the diverging transition zone where the section area increases, at the beginning of the first interface (at the bottom of the loop) between A and B type formulations.

When looking at images of the flow front progression at the surface for the two variants of AB formulations in Figure 5.39-b, it seems that the kinetics of capillary imbibition is slightly faster for P(BA) specimen than that in P(AB) specimen, especially in the horizontal segment at the bottom of the P loop. This is validated by the measured kinetics (slope of the curves) on the graph in Figure 5.39-a. As mentioned in phase I for the analysis of fluid flow front deduced from the line observed at the surface of specimens, it is not clear if the saturation level corresponding to what is observed at the surface is the same for A and B type formulations.

For the BC combination of slurry formulations, we did not succeed in producing P(BC) specimen; only two P(CB) specimens were obtained from the same B01 batch. The results of hexadecane imbibition in these specimens are shown in Figure 5.40.

For the two P(CB) specimens produced in the same batch, the kinetics of hexadecane imbibition shown in Figure 5.40-a is quite similar in spite of the slightly different progression of front flow lines shown in Figure 5.40-b. Again, the geometric dispersion in the contour and thickness of the specimens can explain the discrepancy. In addition, on specimen P(CB)-B01-II, a horizontal crack is clearly seen on the right segment of the P loop. This crack is perpendicular to the direction of the capillary fluid flow. This would tend to cause a deceleration in the rate of imbibition process, as it is observed in Figure 5.40-a for P(CB)-B01-II specimen showing a break in the curve at about 11 000 s. Apart from that effect of the crack, the trend in the imbibition curves is similar to that observed for homogeneous P shape specimens.

Finally, the AC combination of slurries permits to produce two specimens of each P(AC) and P(CA) configurations. The results of capillary imbibition are shown in Figure 5.41.

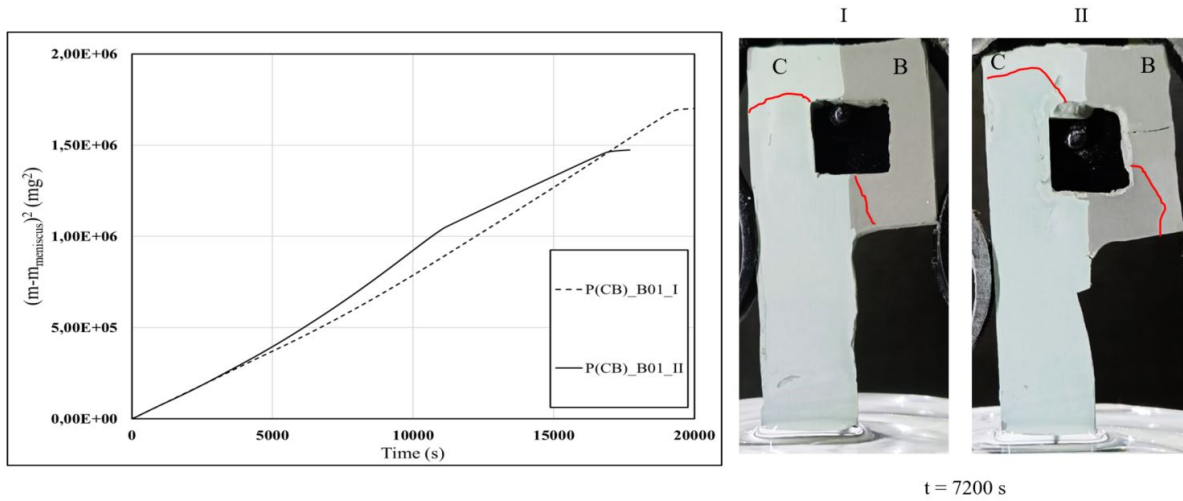


Figure 5.40 a) Progression of capillary imbibition with time for heterogeneous P shape specimens with BC formulations. b) Images of surface flow front (diffuse) for the two heterogeneous P(CB) specimens after 7200 s.

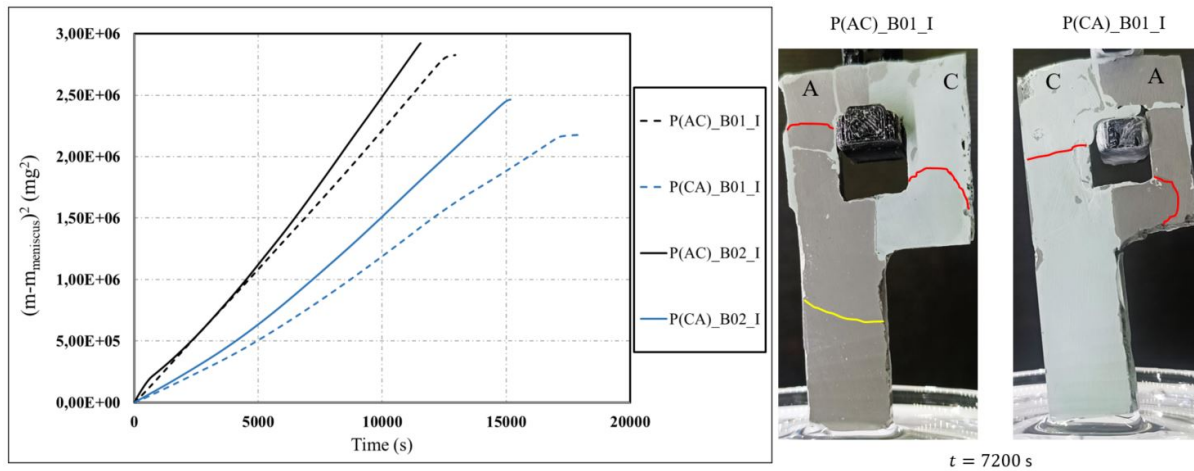


Figure 5.41 a) Progression of capillary imbibition with time for heterogeneous P shape specimens of type AC. b) Images of surface flow front between the two heterogeneous configurations of A and C type microstructure after 7200 s.

In this case, the two specimens for each configurations behave similarly in terms of fluid flow kinetics. It appears that the imbibition kinetics is faster in specimens of type P(AC). This is also apparent in Figure 5.40-b where the fluid flow front lines have progressed on a longer distance in the two branches of the P loop for P(AC) specimen.

Similarly to what was shown for one specimen of P(CB) configuration, the specimens with AC formulations under investigation exhibit transverse cracks that have a substantial impact

on the dynamics of imbibition. These cracks are of a significantly larger scale, which enables them to modify the primary axis of imbibition from longitudinal to transverse. This alteration occurs specifically at the foot of the specimen P(AC)-B02-I, as depicted in Figure 5.41-b. The diffuse surface flow front exhibits greater curvature in the region that is perpendicular to the primary imbibition axis. This translates to a break at the beginning of hexadecane imbibition (Figure 5.41-a). The specimen under investigation exhibits transverse cracks that have a substantial impact on the dynamics of imbibition. Another example of the effect of crack on the deceleration of flow kinetics is shown in specimen P(CA) close to the top right corner of the P loop (Figure 5.41-b), resulting in a break of the imbibition after about 12 000 s in Figure 5.41-a.

The observation of the volume flow front, obtained by X-ray tomography after interrupted capillary imbibition by *exo*-DCPD, provides preliminary indications of the behavior of the flow front when it crosses the interface between the two formulations. Figure 5.42 displays typical fluid progression in two heterogeneous P shape specimens.

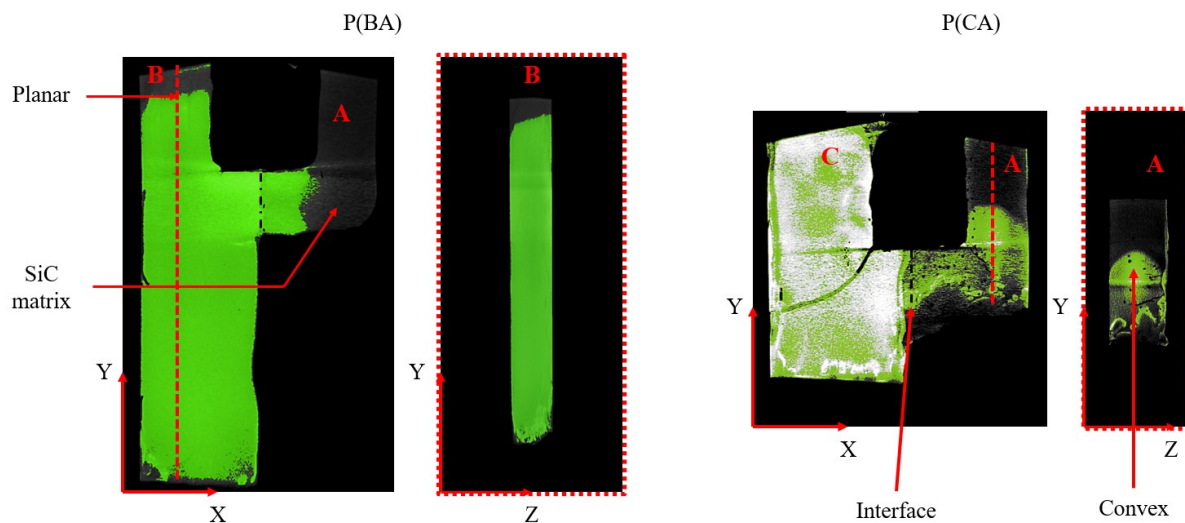


Figure 5.42 Volume flow front that is generated for the heterogeneous P shape configuration near the interface. Left: P(BA) specimen; right: P(CA) specimen. Here the dotted red line denotes the orthographic section of the adjacent view for the P shape.

The first thing to notice on these images is the change in the intensity of X-ray detection from one slurry formulation to the other, on both sides of the interface. This could be related to the variation in the level of porosity between the two formulations or to the level of saturation between the two formulations, or a combination of these two phenomena. For specimen P(CA) (Figure 5.42, right), it is clear that the cracks that are present at two locations in the horizontal segment of the P loop are not totally filled by the capillary fluid, indicating a

retardation of capillary flow in presence of macroscopic defects.

Simulation of capillary imbibition in heterogeneous specimens

The simulation of capillary flow in heterogeneous P shape specimens with FlexPDE causes some numerical problems due to the radius of curvature at the bottom of the P loop where the interface between the two formulations is also located. For that reason, a simplification was adopted for the definition of the contour of the geometry: a sharp corner was used instead of a radius of curvature.

The simulation was carried out by considering the P(AC) and P(CA) configurations since they are those showing a clear separation of capillary kinetics, as shown in Figure 5.41. As it was done before, the properties of both porous media (ε and d_{50}) that were used for the simulation came from Table 5.11. The values for tortuosity τ and Van Genuchten parameter n are the same as those found in phase I. The results of simulation of capillary hexadecane imbibition are shown in Figure 5.43 for a simulation time of 7200 s corresponding to the time of experimental imbibition shown in Figure 5.41-b.

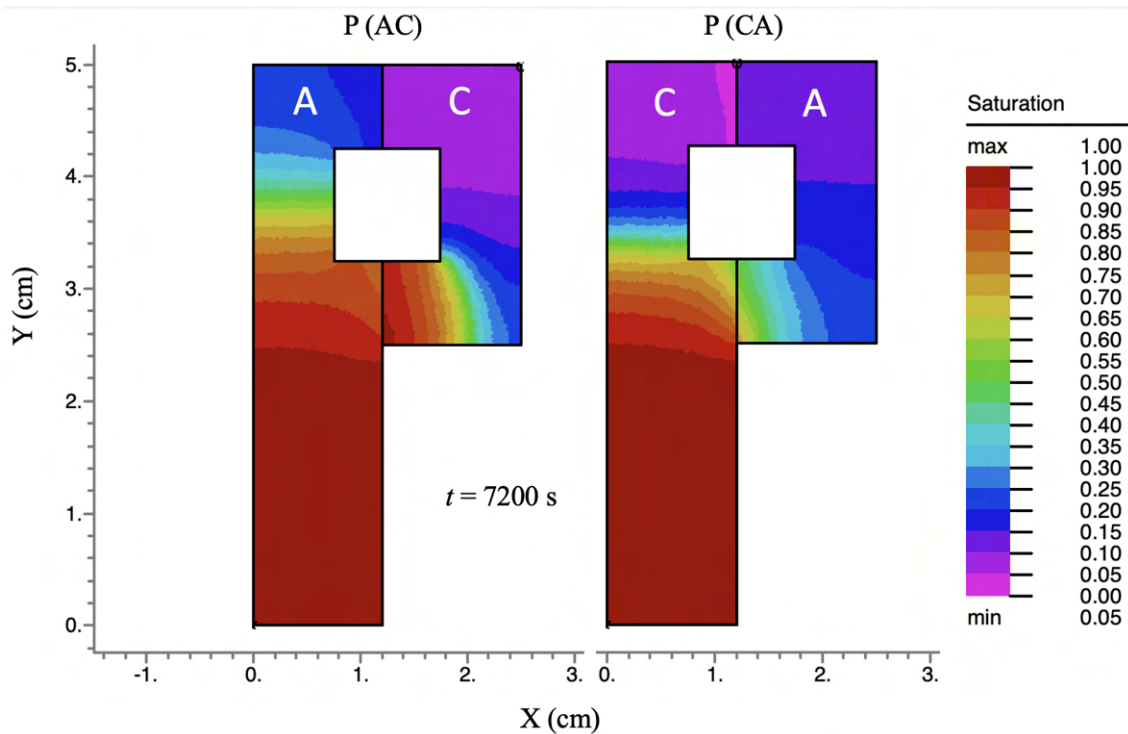


Figure 5.43 Saturation color plot for simulated capillary flow of hexadecane in heterogeneous P(AC) and P(CA) specimens. Simulation time = 7200 s.

In terms of capillary flow front detected at the surface of the specimens (Figure 5.41), it

seems that the flow kinetic is fastest in specimen P(AC) compared to specimen P(CA). This is what is observed in simulation results by FlexPDE shown in Figure 5.43. If we interpret the position of the flow front from the position of the saturation level of 50 % (green color), the flow front progressed further in specimen P(AC). These results are corroborated by the simulated mass gain as a function of time shown in Figure 5.44. For these graphs, the simulation was stopped at 7200 s. Again it is clear that the capillary flow kinetics is fastest in P(AC) specimen. Also, the overall mass gains in both specimen configurations evaluated from the simulation (Figure 5.44) and measured experimentally (Figure 5.41) are in quite good agreement. The most interesting phenomenon that could be detected from Figure 5.44 is a slight change of slope between 4000 and 5000 s, corresponding to the time where the flow front arrives close to the first interface at the bottom of the P loop. For P(AC) specimen, the slope (and then the capillary flow kinetics) increases while for specimen P(CA), the slope decreases.

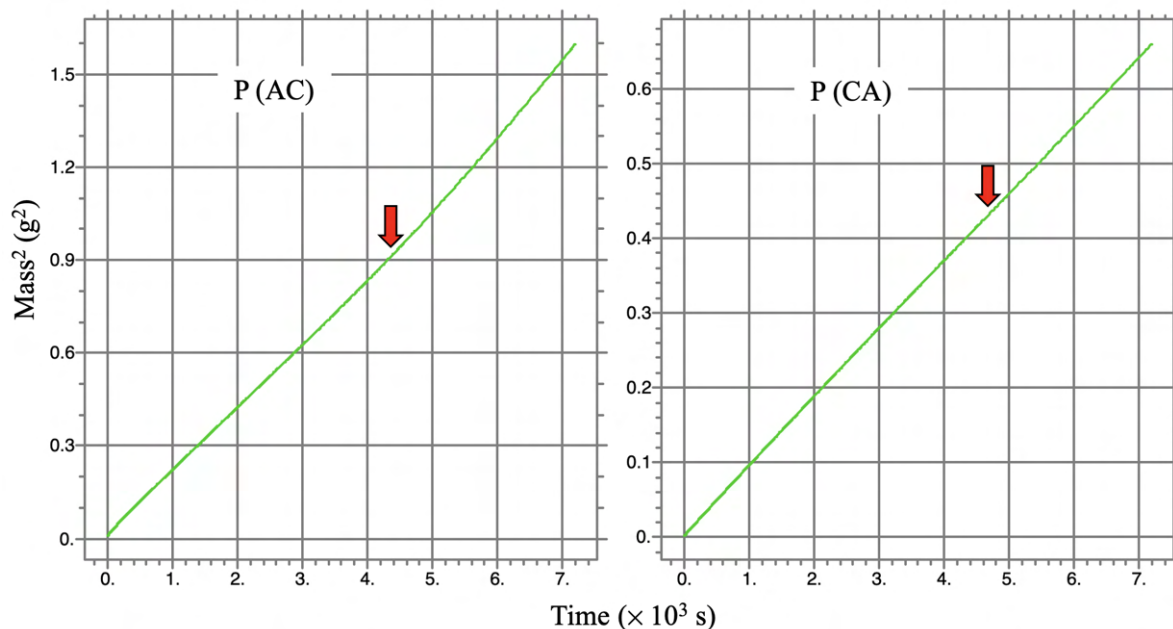


Figure 5.44 Evolution of square of mass as a function of time for simulated capillary flow of hexadecane in heterogeneous P(AC) and P(CA) specimens. Red arrows indicate slight change of slope.

When the flow front arrives at the transition zone at the bottom of the P loop, it meets the interface with a flow direction that is not exactly perpendicular to the interface between the two porous media. In the present case, with the properties given in Table 5.11, it appears that the d_{50} value of formulation C is slightly lower than that of formulation A, signifying that the (negative) capillary pressure on side C is higher. This could explain the difference

that is observed in the kinetics of capillary imbibition in both types of specimens. For P(AC) specimen, the capillary fluid flows first in A leg before it arrives close to the interface. When the fluid is exposed to the stronger capillary pressure on side C, it is pulled by the C porous medium causing an acceleration of the imbibition kinetics (Figure 5.44) and a temporary depletion of liquid on the A side, as shown in Figure 5.43. After a certain time, the depletion is filled on the A side because the flow velocity on the C side is lower due to larger flow resistance caused by smaller d_{50} . In P(CA) specimen, the behavior is reversed. When the flow front arrives near the interface after having progressed in the leg of formulation C, it sees medium A with lower capillary pressure than that on C side. The driving force for passing through the interface is then reduced, causing a retardation of the flow front to cross the interface and a deceleration in the imbibition kinetics (Figure 5.44). If the difference in median pore size between the two porous media had been more important, the acceleration and deceleration of kinetics would have been magnified.

5.3.3 Concluding remarks for phase III

Some preliminary experiments were carried out in order to define the actual geometry of specimens for phase III. The goal was to test two capillary flow features in the same specimen geometry: diverging/converging flow and flow through heterogeneous media. The P shape specimens that has been finally selected provide some advantages but also some problems that limit the extent of results that it could produce.

For the first part of the experiments on homogeneous P shape specimens, the aim was to verify if the widening of the section area causing diverging flow could lead to incomplete imbibition on certain zones of the part. The capillary imbibition experiments and the numerical simulations with FlexPDE did not permit to arrive at that conclusion for the actual P shape geometry. In all cases, the porous media happens to be filled after a certain time, if we suppose that the supply of wetting liquid is continuous. The experiments that were done with other geometries (not presented in this thesis) gave the same result. The main reason is probably associated with the limited section area ratio that could be practically obtained with the fabrication processes (molds, furnace, injection devices, ...) developed at Polytechnique.

The second part of the experiments with heterogeneous P shape specimens provided better results in terms of the effect of interfaces on the capillary imbibition. The overall capillary flow kinetics is conditioned by two main parameters: driving force (capillary pressure) and viscous flow resistance. Both of these parameters depends strongly, in opposite effect, on the pore size. If the porous medium with smaller pore size generates more driving force (higher suction capillary pressure), it causes also larger flow resistance.

In the present experiments, when the fluid flow front arrives close to an interface between media having different values of d_{50} , acceleration or deceleration of capillary flow can be observed depending if the pore size decreases or increases across the interface, respectively. This could cause momentarily depletion or accumulation of fluid in the medium located before the interface. This effect tends to reach equilibrium with time as the pressure evolves being more uniform through the porous media.

The transformation of matrix geometry occurs when the initial uniform cross-section rectangular specimen progresses towards a more intricate shape, with a transition zone that exhibits the division of the imbibed flow channel into two distinct channels.

5.4 Impact of heterogeneous granular compaction: phase IV

The main objective of this phase is to examine the capillary flow behavior along an interface separating two different poral networks. The bi-laminar configuration of the specimens consists in two layers of dissimilar slurry formulations side by side, with an interface parallel to the main direction of the capillary flow. This specimen geometry bears resemblance to a bi-disperse model utilized in the study of capillary imbibition and described in Section 2.6.5. In this model, two adjacent capillary tubes of different dimensions are joined, permitting the fluid to cross freely the interface between the tubes. Since the interface between the two layers of the bi-laminar specimens does not impede the fluid flow in the transverse direction with respect to the main direction of the capillary flow along the specimens, this design of geometry would permit to characterize the capillary flow in heterogeneous pore structures.

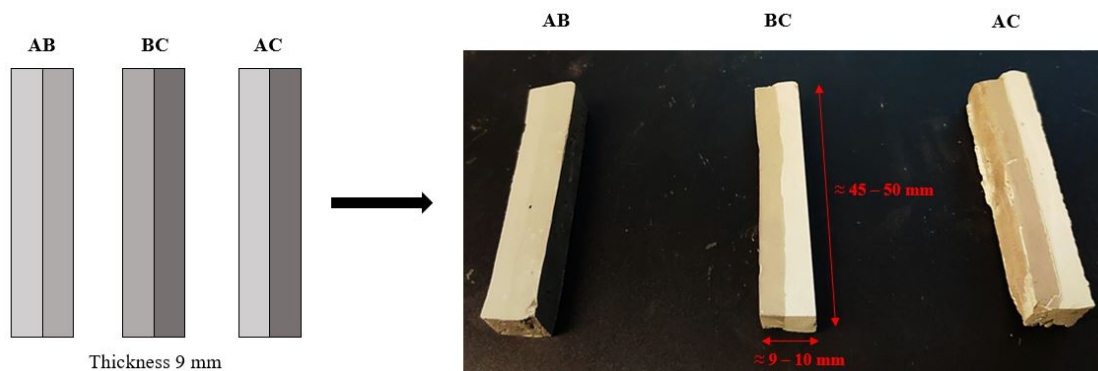


Figure 5.45 Matrix geometry fabrication plan and the actual bi-laminar specimens.

For this study, three different pairs of specimens were fabricated by combining the slurry formulations of types A, B and C. The schematic of the fabrication plan and the typical specimens are shown in Figure 5.45. It should be reminded that the two formulations A and

B are obtained from the same SiC powder type. This explains the very light contrast in the visual definition of the two layers. The slurry cast mold was set to produce specimens of nominal thickness (parallel to the interface) of 9 mm. The width of the specimens includes two layers of 4.5–5 mm for a total of 9–10 mm.

The production of bi-laminar specimens initially exhibited variations in layer thickness of the two formulations. The fabrication methodology was improved to obtain a ratio of fifty percent for each formulation. Another crucial aspect to consider in this context pertains to the nature of the separating interface within the matrix. As depicted in Figure 4.30, the method of producing bi-laminar specimens leads mostly to continuous interface where no obstacle is visible to impede the passage of capillary fluid from one porous media to the other. In some rare cases, a crack was detected along part of the interface. Since this type of crack is aligned parallel to the capillary flow, it should not reduce the capillary imbibition kinetics, except for a limitation in transverse flow (perpendicular to the interface).

5.4.1 Characterization of bi-laminar specimens

The characterization of bi-laminar specimens in terms of the poral network was carried out by MIP on samples coming from three distinct locations; this is shown in Figure 5.46. For example, for a bi-laminar specimen AB, noted BL(AB), one sample was extracted at the interface for characterizing the combination of the two formulations. Two other samples, noted BL(AB)/A and BL(AB)/B were extracted on the A and B sides respectively.

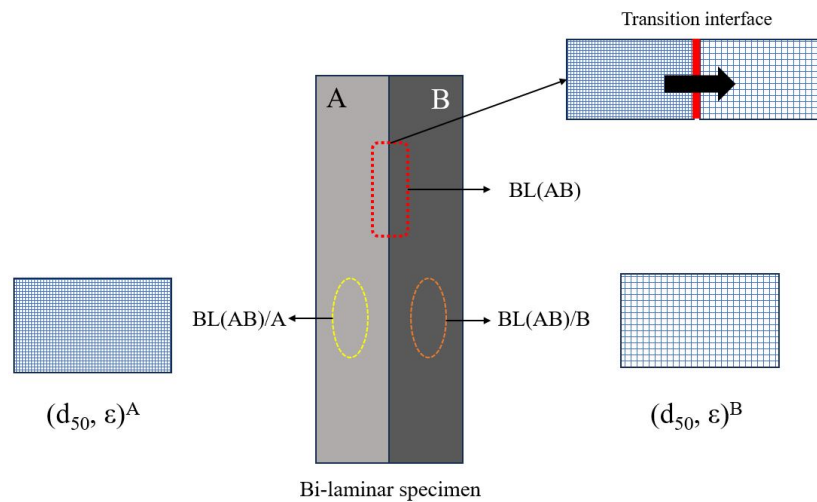


Figure 5.46 Identified zones for the extraction of samples for characterization of microstructure for bi-laminar specimens.

MIP experiments on the three zones for each bi-laminar type of specimens give the pore size distribution curves shown in Figure 5.47. Contrary to what was observed at the interface of heterogeneous P shape specimens of phase III, the samples at the interface of bi-laminar specimens do not show two peaks clearly separated, except for BL(AB). This is probably due to the close values of d_{50} for both formulations in each bi-laminar configurations. The MIP experiments also permitted to evaluate the level of porosity for the three zones of each specimens. Even if the values of d_{50} and ε for each formulation could be significantly different from those evaluated in phase I, the ranking for the three formulations follows the same tendency. All these results coming from MIP are given in Table 5.12. Also given in Table 5.12 are the porosity values measured by triple weighing over the entire volume of the bi-laminar specimens.

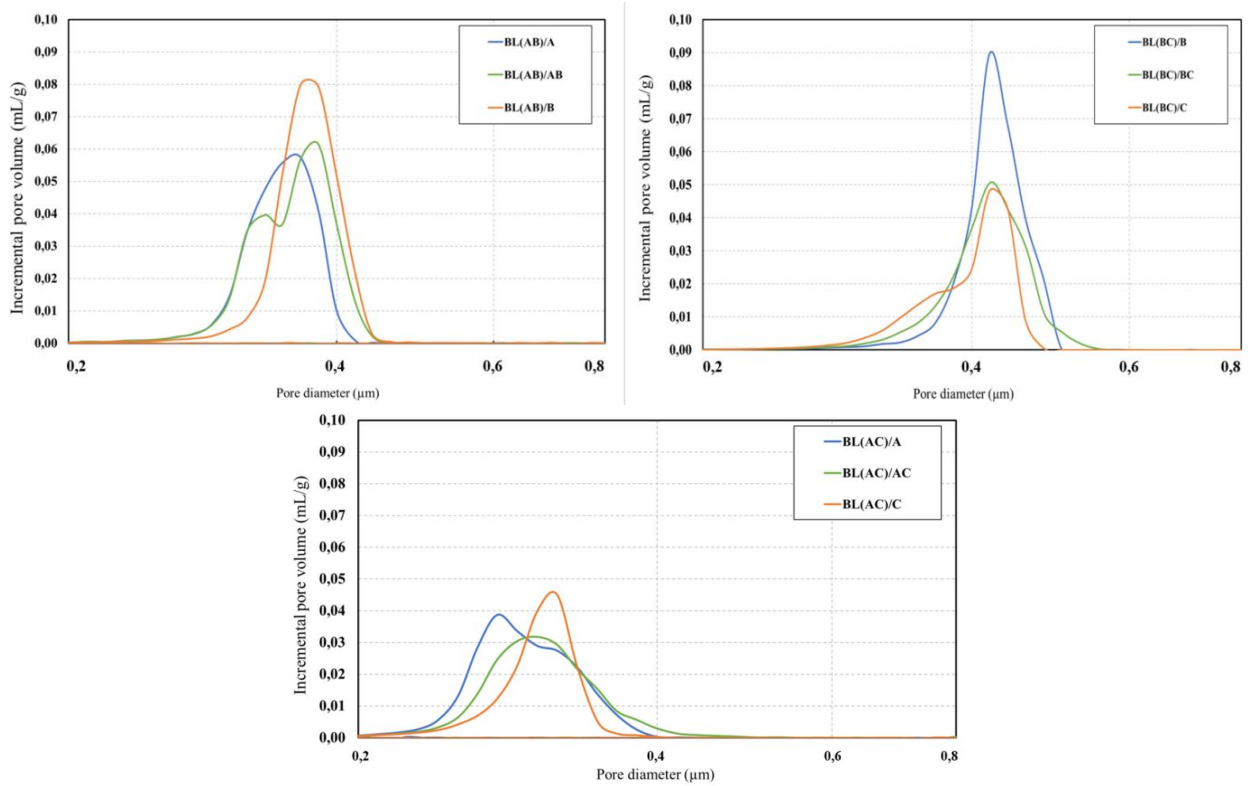


Figure 5.47 MIP characterization of microstructure for the three bi-laminar configurations. For each AB, BC and AC configuration, the characterization was carried out in three zones.

When comparing the values of porosity for the whole specimens (Twe) with that obtained by MIP for the sample extracted at the interface, there is quite good agreement since the bi-laminar specimens were fabricated while targeting a 50–50 % proportion of the two formulations. However, since the local values of pore network parameters are significantly different from those obtained in phase I, no clear comparison could be made between specimens of

Specimen	ε [Twe] (%)	ε [MIP] (%)	d_{50} (nm)
BL(AB)	49.52 ± 0.57	50.65	370
BL(AB)/A	–	50.65	357
BL(AB)/B	–	52.10	381
BL(BC)	44.77 ± 0.19	42.85	419
BL(BC)/B	–	50.04	444
BL(BC)/C	–	21.76	395
BL(AC)	39.57 ± 0.06	39.82	314
BL(AC)/A	–	44.35	300
BL(AC)/C	–	35.82	315

Table 5.12 Pore network parameters for the bi-laminar specimen configurations with the values coming from the three zones defined in Figure 5.47.

different phases.

5.4.2 Capillary rise experiments: bi-laminar specimens

Capillary imbibition experiments with hexadecane were conducted on all bi-laminar specimens. The kinetics of liquid mass impregnation was characterized by means of $m^2(t)$ curves showing mostly straight lines since the section of both formulations is constant through all the experiment as the flow progresses. For the three configurations of bi-laminar specimens, the results are shown in Figures 5.48 to 5.50.

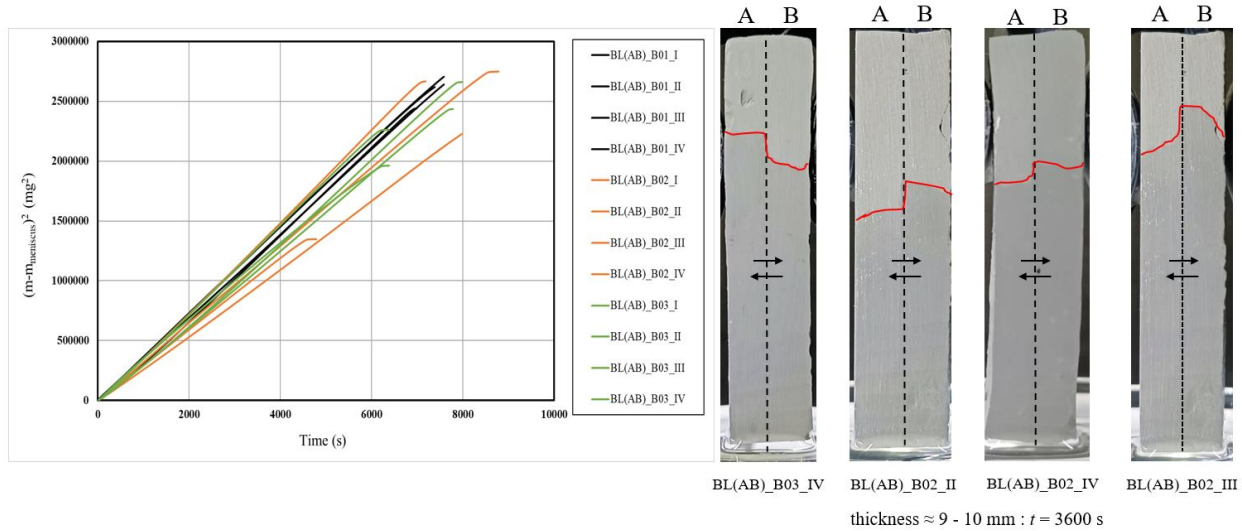


Figure 5.48 Capillary imbibition results for bi-laminar AB configuration. Results from all the specimens produced in batches B01, B02 and B03.

Figure 5.48 gives the capillary imbibition curves for all the BL(AB) specimens produced through three different slurry cast batches. It is clear that the fabrication of the specimens is highly reproducible from one batch to another, since the dispersion between the curves is low. The dispersion in the results is also very low within a same batch, except for batch B03 where the gap between the specimens showing the fastest and slowest kinetics is the most important. For all the specimens, the kinetics are characterized by straight lines indicative of a diffusive phenomenon described by typical Washburn's law.

For three different specimens shown on the right side of Figure 5.48, it appears that the presence of the interface plays an important role on the kinetics of fluid flow in the porous media located on both sides. In some cases, the overall fluid flow kinetics is faster on the B side while it is less clear for specimen I. As mentioned in the analysis of results of phase I for individual pore network formulation, the fluid flow kinetics depends on all the parameters that characterize the porous media, namely the porosity, the median pore size and the tortuosity. In addition to the influence of porous medium, its neighbor has an effect to curve the surface flow front line near the interface.

Similar results were obtained for bi-laminar specimens BL(BC), as shown in Figure 5.49. In this case, the dispersion between results coming from specimens of batch B02 is more important. For some specimens of both batches, the kinetics is not exactly described by straight lines, that could indicate the presence of some defects (cracks) that could modify the flow path. This could possibly be explained in part by the difficulty in elaborating slurry cast specimens from the type C formulation as explained before.

What is interesting however is the strong tendency to develop similar flow front profile with faster kinetics on the C side (see images on the right of Figure 5.49). When taken separately (as demonstrated in phase I), it seems that there is a reversion of behavior in terms of flow front progression kinetics. As shown also in specimens BL(AB), the flow front line near the interface is deflected, indicative of interaction between the flows on both sides of the interface. Since the interface is not impeding the transverse flow, the resulting equilibrium should be influenced by the capillary pressures (related to d_{50}) on both sides of the interface.

Finally, only a single batch of specimens was slurry cast for specimens BL(AC). The results of imbibition kinetics are shown in Figure 5.50. The kinetics are well represented by diffusive phenomenon characterized by straight $m^2(t)$ lines. For the two specimens B01-I and B01-II, the position of the flow front line detected from the surface is almost the same on A and C sides, except for some variations near the free surfaces and close to the interface.

The consolidated matrix exhibits multiple flaws distributed throughout its volume, which in turn impact the overall process of capillary imbibition. The existence of macro-defects and

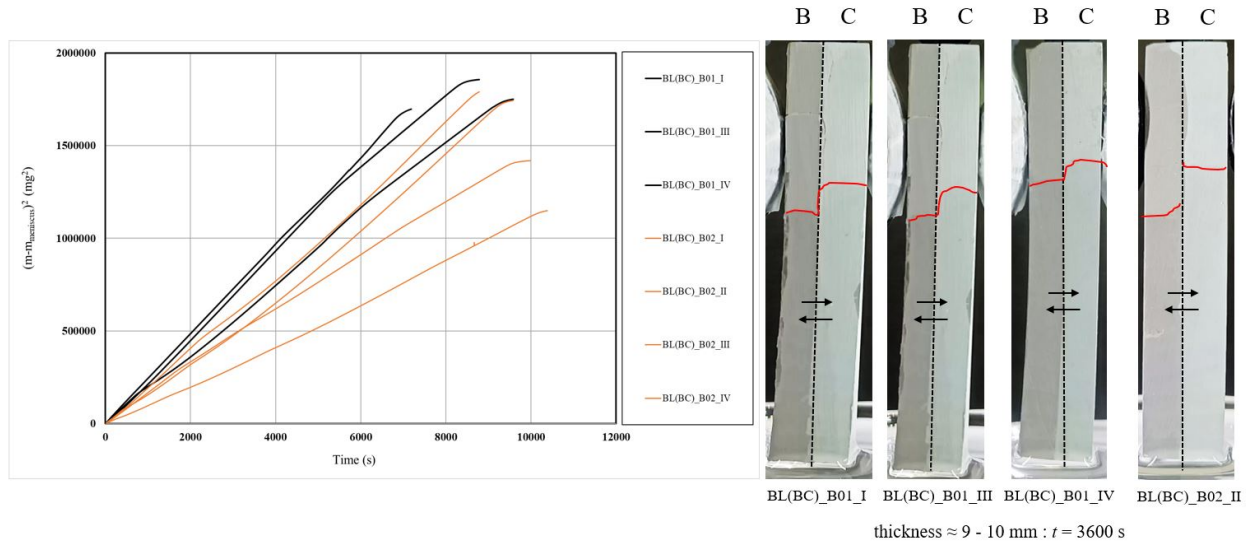


Figure 5.49 Capillary imbibition results for bi-laminar BC configuration. Results from all the specimens produced in batches B01 and B02.

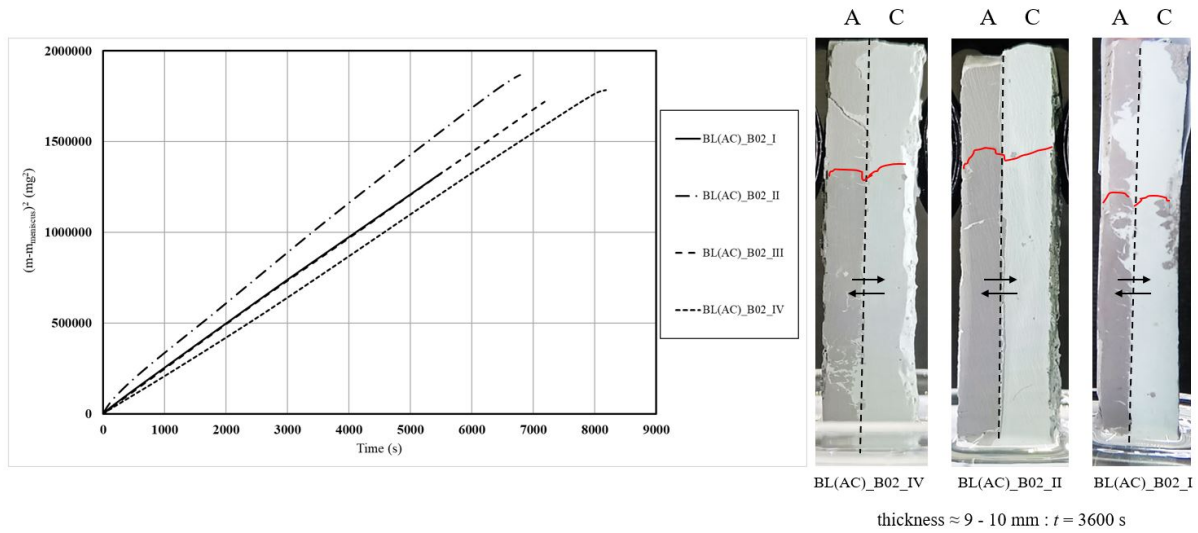


Figure 5.50 Capillary imbibition results for bi-laminar AC configuration. Results from all the specimens produced in a single batch B01.

irregularities contributes to increased randomness within the poral network that is formed during the fabrication process of the SiC matrix.

Figure 5.51 provides clear evidence of significant matrix defects. Clusters of macro-pores can give rise to the presence of both longitudinal and transverse macro-cracks. The occurrence of both longitudinal and transverse cracks can be ascribed to the differential rate of contraction that arises from the process of air drying followed by high-temperature heat treatment of the

consolidated SiC matrix.

When looking at the flow front on both sides of the interface with the help of X-ray tomography, it is possible to observe the same features that were characterized in homogeneous specimens of phase I. Figure 5.52 shows the flow front in BL(AB) specimen. On the front view parallel to the interface (image at the center), it is clear that there is an abrupt jump of the flow front at the interface where the progression is faster on B side for this moment of interruption of the capillary rise experiment with *exo*-DCPD. On both sides of the interface, in materials of types A and B, we see that the flow fronts observed perpendicularly to the interface (at the plane of cut illustrated in the center image) demonstrate a parabolic shape as those observed in phase I. It is also interesting to note that on side B, the clusters of pores are not filled with the *exo*-DCPD resin. From previous experiments by Floriane Dewart [140] in her master thesis research, it appeared that this phenomenon is observed until the end of the capillary imbibition experiments. This will be discussed in more details in Chapter 6.

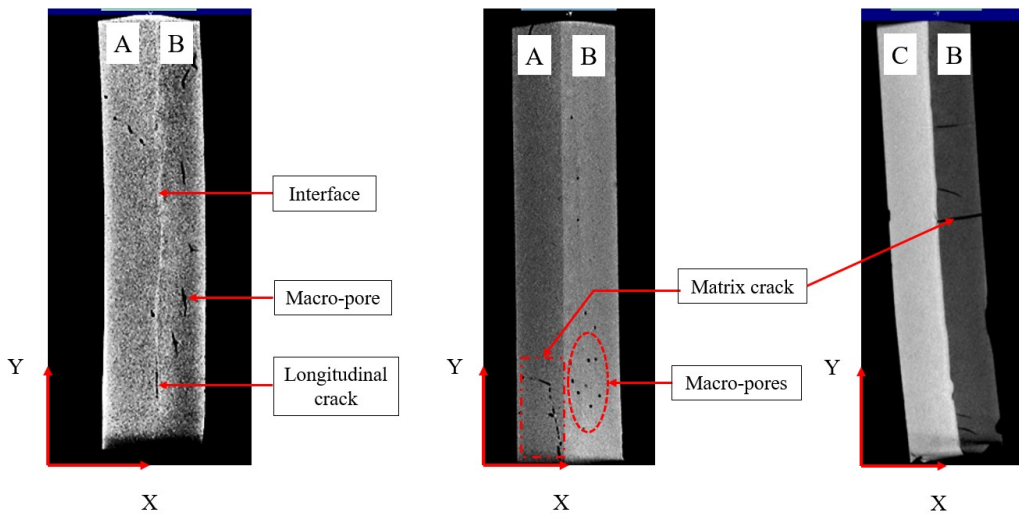


Figure 5.51 Presence of various classes of defects in the bi-laminar specimen.

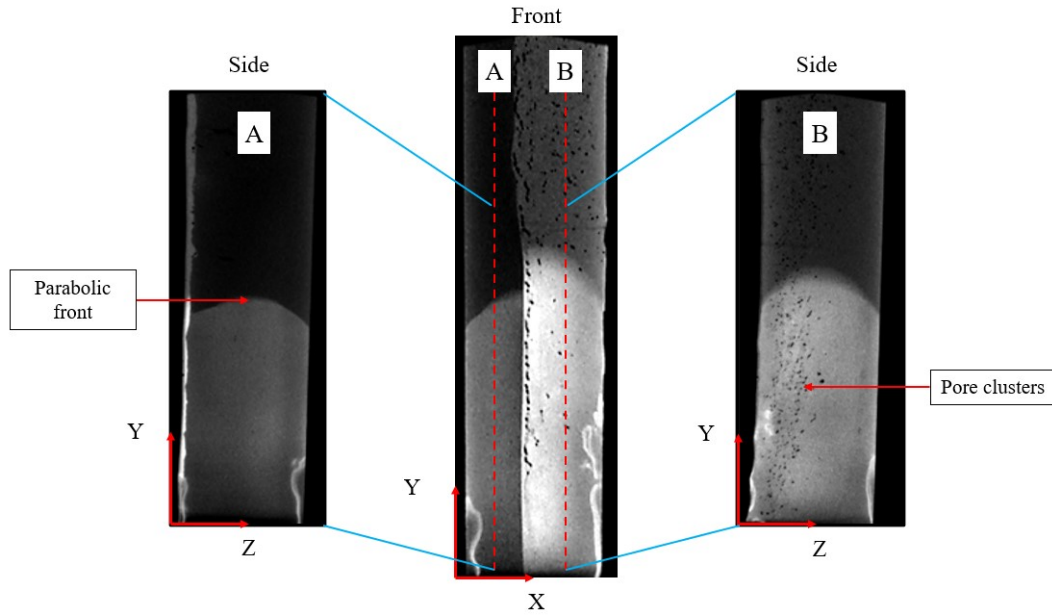


Figure 5.52 Parabolic volumetric flow front observed on both sides of the interface for bi-laminar AB specimen. The transverse direction also generates the parabolic flow front when observed from the side.

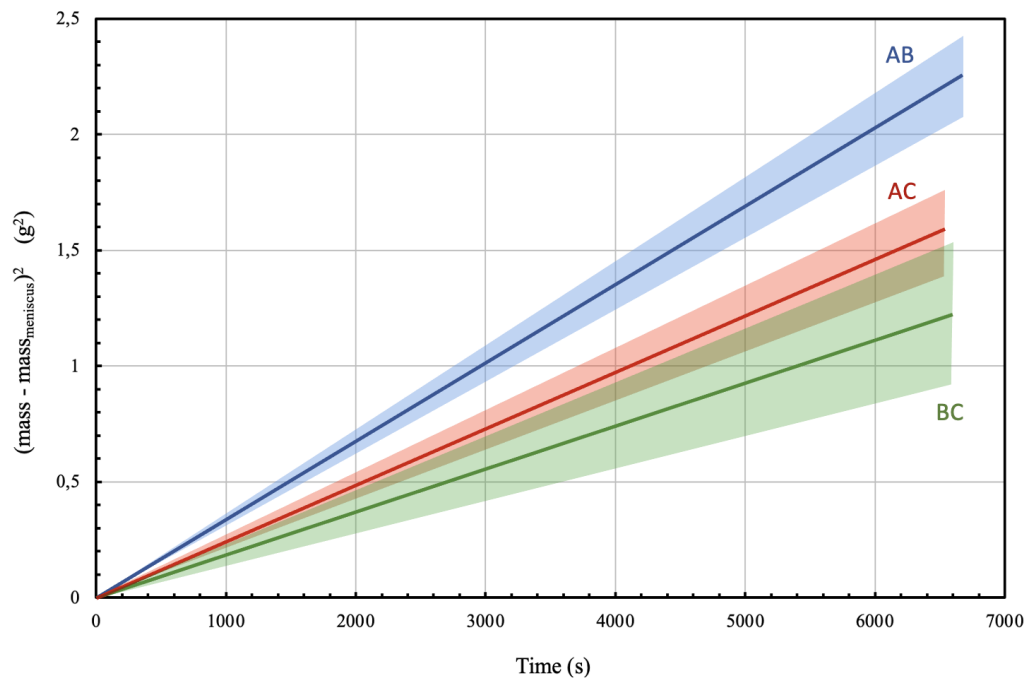


Figure 5.53 Comparison of averaged imbibition rates for the three bi-laminar configurations. The light areas around the averaged straight lines show the standard deviation on the slope of the curves.

To summarize all the capillary tests carried out on bi-laminar specimens, Figure 5.53 shows the averaged $m^2(t)$ lines obtained from the three configurations. Even if the pore network characteristics of a given slurry formulation are different in two variants of bi-laminar configurations (for example, type A formulation in BL(AB) and BL(AC)), it is interesting to note that the behavior of the three various configurations are significantly different. For BL(BC) specimens, the dispersion is more important than for the two other configurations.

5.4.3 Simulation of imbibition for bi-laminar configuration

For heterogeneous specimens such as those of phase III and phase IV, it is difficult to characterize experimentally the tortuosity and Van Genuchten parameters since what would be obtained are averaged values. The bi-laminar specimens possess an individual layer thickness of each formulation that is approximately 50 percent of the total width ($\approx 9\text{--}10$ mm). Considering that the thickness of the bi-laminar specimens (measured in a direction parallel to the interface) is in the order of 9 mm, this makes specimen section that is almost squared. The total section of the specimens would then be large enough to consider the microstructural properties to be similar to the specimen formulations from phase I. So for the simulation of the capillary flow behavior in bi-laminar specimen with FlexPDE, the input values of tortuosity and Van Genuchten parameter n for each pore network formulation were the same as those used in phase I. For the values of d_{50} and porosity ε characterizing each formulation of the bi-laminar specimens, those given in Table 5.12 serve as reference.

The boundary conditions for bi-laminar geometry are similar to what was defined for heterogeneous P shape specimens of phase III. The condition at the interface between the two layers enables the inter-layer transfer of fluid. The junction of two layers develops the transition boundary where the change in median pore size, tortuosity, porosity, and corresponding Van Genuchten function occurs.

The advancement of the surface flow front demonstrates variations in the imbibed height, resulting in discernible disparities in distances on both sides of the interface. The simulation conducted using FlexPDE also demonstrates slightly different imbibition kinetics in both layers. The presence of inter-layer diffusion leads to the observation of deflection of flow front lines near the interface that is not present in the simulation of homogeneous pore structures. Typical simulation results and the corresponding images of flow front lines in bi-laminar specimens are shown in Figure 5.54.

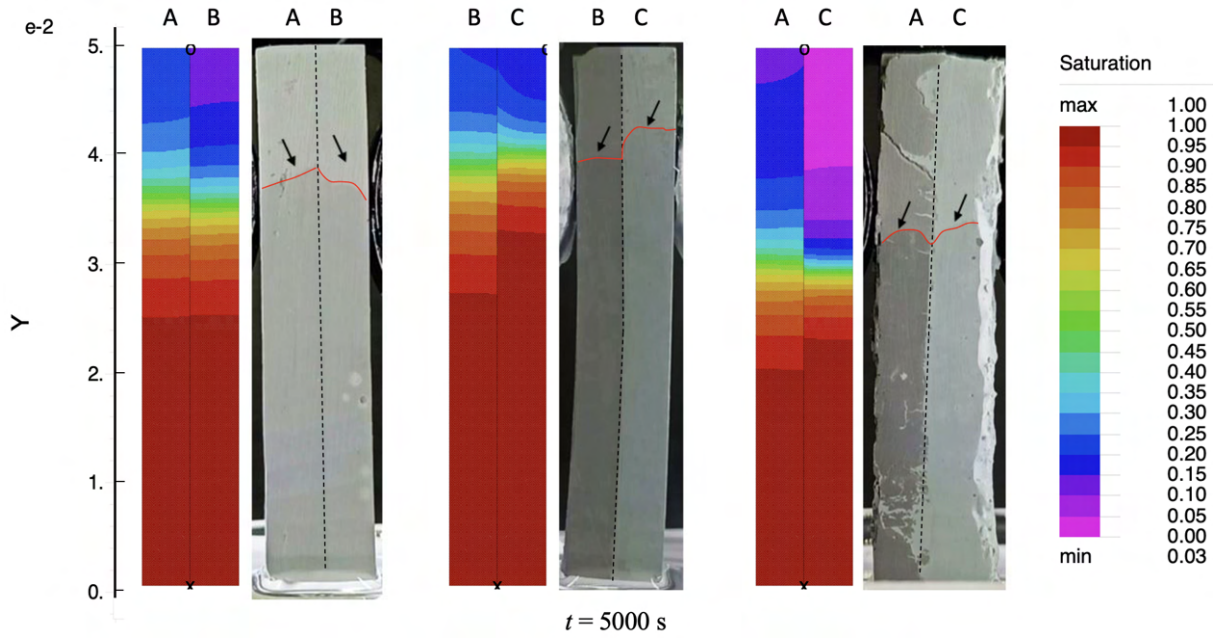


Figure 5.54 Comparison of experimental diffuse type surface flow fronts and contours of saturation obtained by simulation for the three configurations of bi-laminar specimens of phase IV. The simulated and experimental times correspond to 5000 s.

The trend that could be pointed-out from both, the simulation and the experiment, is that capillary flow front speed in each layer of a bi-laminar specimen seems to be opposite to what was observed separately in homogeneous specimens of the same formulations. For example in Figure 5.54, the flow front line in layer C of BL(BC) progressed further than that in layer B. It was clear in the phase I that specimens of type B showed the fastest capillary kinetics. The same trend is observed in specimens BL(AC) and BL(AB), but to a lesser extent since the difference in the pore characteristics are smaller.

When the experimental results are compared to the results of simulation for the same time of imbibition (5000 s in this case), it appears that, as observed in the previous phases, the positions of the surface flow front (SFF) lines on all specimens correspond to the saturation level of 50–55 % marked by the light green color. This trend seems to be one practical way to interpret the results of FlexPDE in the solving of Richards equation.

As it is well known, the main driver for capillary flow is the capillary pressure (Young-Laplace Equation 2.6) that is inversely proportional to the capillary tube diameter. It means that the smaller is the d_{50} , the larger is the capillary pressure to force the impregnation of a liquid. However, the pore size diameter has a negative effect on the kinetics of capillary flow: the smaller the diameter, the stronger the viscous force causing resistance to capillary flow.

During the capillary rise experiment, the distribution of pressure evolves continuously along the porous bi-laminar specimens. As shown in Figure 5.55, the simulation of capillary flow in bi-laminar BL(BC) specimen gives the pressure contours for different time during the test. At the very beginning of the experiment (20 s), the (negative) pressure profile gives higher values on the C side, where the d_{50} is smaller. As the experiment time progresses to 100, 500 and 3000 s, the pressure on both sides of the interface tends to reach equilibrium. In parallel, the position of the flow front on both sides could be visualized approximately by the position of the green level of pressure. If the level is about the same in terms of pressure, it is different in terms of saturation level, showing a net higher value on the C side (Figure 5.56). The higher level of fluid front on the side of higher capillary pressure can be explained by the transverse flow coming from the B side, where the flow resistance is lower, towards the C side, where the (negative) capillary pressure is higher. A similar tendency was observed by Bico and Quéré [63] where the level of fluid is higher in the tube with smaller diameter. The bi-laminar specimens then act as a bi-disperse media.

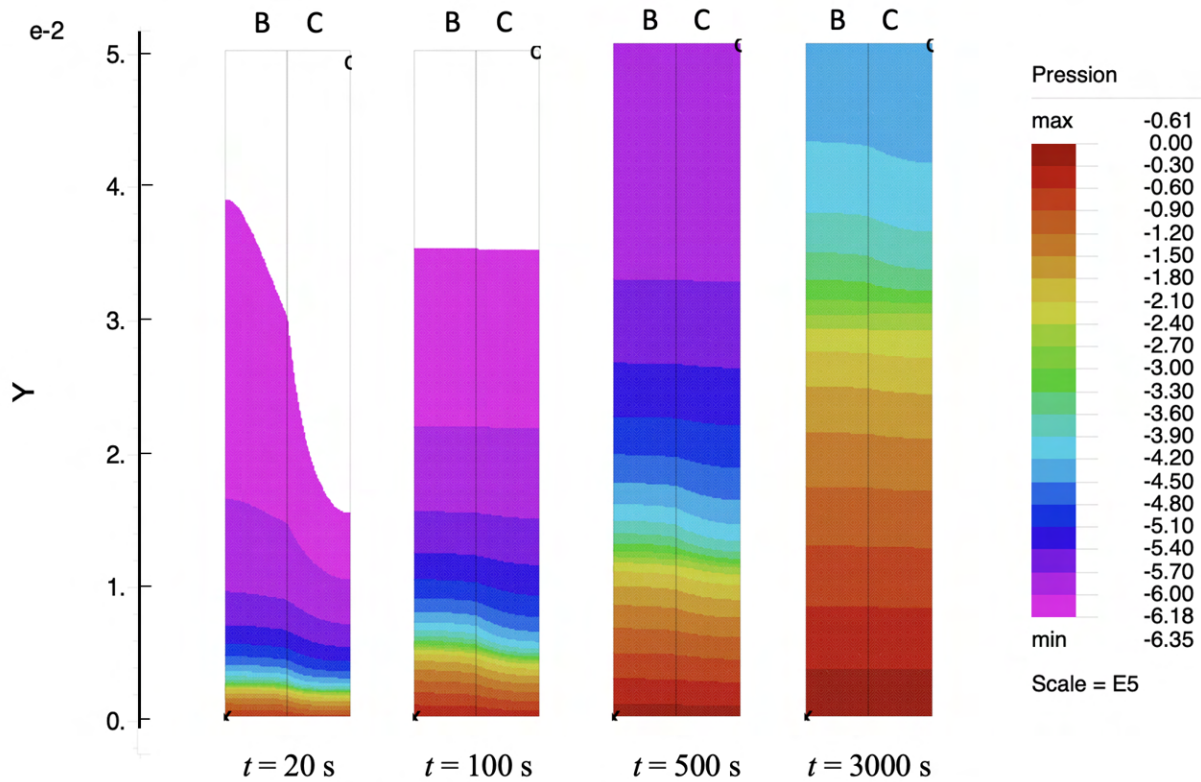


Figure 5.55 Distribution of pressure in bi-laminar specimens BL(BC) for different times of imbibition.

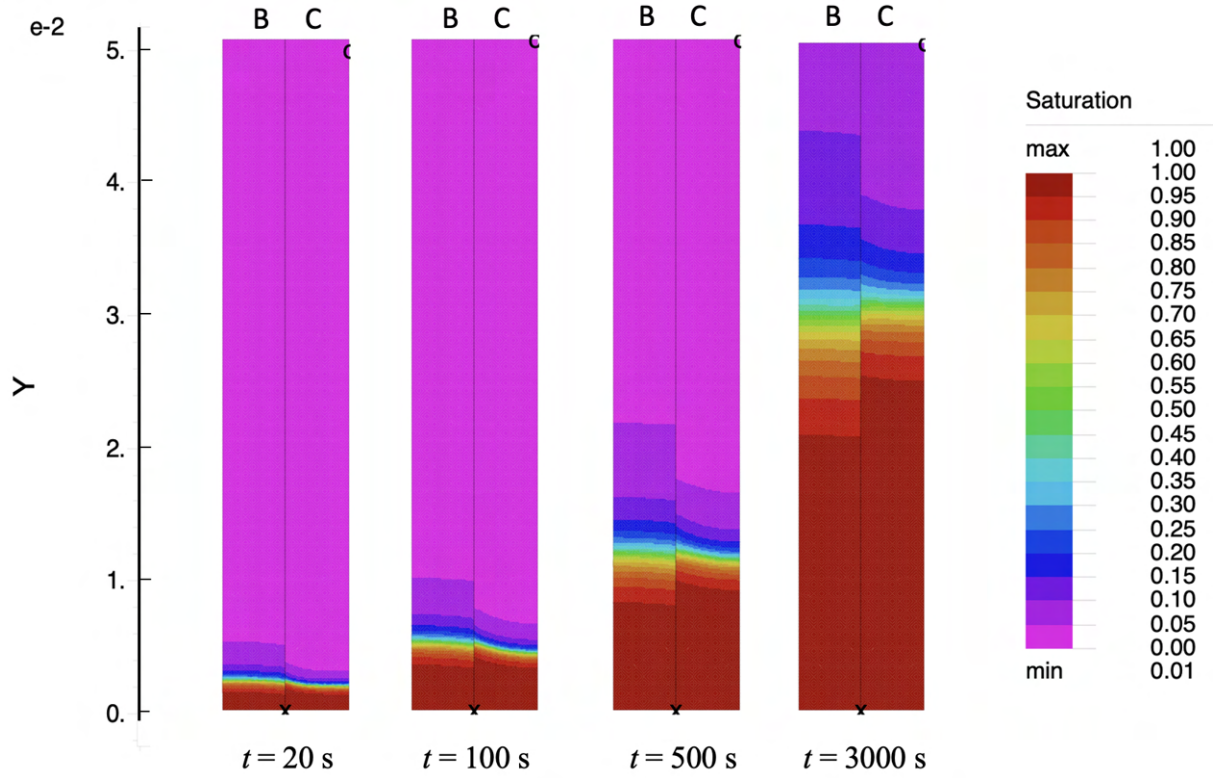


Figure 5.56 Distribution of saturation level in bi-laminar specimens BL(BC) for different times of imbibition.

5.4.4 Concluding remarks for phase IV

The goal of phase IV was to evaluate the effect of heterogeneous bi-laminar structure on the capillary imbibition kinetics. The comparison between the results obtained from the capillary imbibition experiments and those resulting from the simulation with FlexPDE are quite satisfactory in a sense that both show the same trend in the relative capillary kinetics in the two layers of bi-laminar specimens with the interface between the two pore network formulations being parallel with the main direction of fluid flow. Similar in principle to the bi-disperse media arrangement proposed theoretically by Bico and Quéré [63], the bi-laminar configuration favors a fluid path from the most permeable medium with transverse flow (perpendicular to the interface) to the medium showing higher resistance to the flow due to its smaller pore size.

For the fluid flow to occur, two conditions should be satisfied. The first one is that it should be favored energetically; this translates to the effect of capillary pressure which is the driving force (energetic condition) for the fluid flow. The second condition is based on the kinetics: the mechanical resistance to the flow (viscous force) should be low enough to permit fluid flow.

The assembly of these two conditions can explain why transverse flow develops perpendicular to the interface, in the direction of increasing (negative) capillary pressure and through the medium having the highest permeability.

CHAPTER 6 DISCUSSION ON CAPILLARY FLOW IN HETEROGENEOUS POROUS MATERIALS

The production of SiC/SiC ceramic matrix composites (CMC) involves a sophisticated procedure that requires meticulous precision and control. This process is designed to achieve the necessary high-temperature resistance required for components operating in environments where there is a heightened risk of failure due to elevated temperatures. SiC-based ceramic matrix composites currently offer a favourable weight reduction while maintaining overall strength, rendering them a viable alternative to high-performance materials such as superalloys.

To obtain the particular properties expected for SiC-based CMC, one important step in the processing of the material involves capillary imbibition of the granular SiC matrix by liquid silicon. The success of this melt infiltration processing step is directly related to the capacity of the fluid to fill completely the pore network. We will discuss in this Chapter 6 how the morphology and characteristics of pore network influence the capillary imbibition of SiC/SiC CMC.

6.1 Context of ceramic matrix composites fabrication

This research study focuses on the matrix phase of ceramic matrix composites (CMC) and examines the capillary imbibition dynamics of the matrix, specifically investigating how variations in morphological parameters and pore network characteristics affect this process. The research work has relied mainly on fabrication process step named melt infiltration (MI), where liquid silicon is infiltrated by capillarity through the granular matrix.

The typical microstructure of a SiC/SiC CMC was shown previously in Figure 2.12. Figure 6.1 reproduces schematically all the various morphological and pore network characteristics that could influence the capillary imbibition mechanisms during MI step. As explained in Section 2.3.2, the CVI coating deposited before the slurry cast step has the effect to close the intra fiber tow structure, impeding the infiltration of fine SiC particles during slurry cast step and liquid silicon during the melt infiltration step. This results in a network of granular matrix channels of different sizes distributed in the inter-tow regions. For different reasons, the slurry cast step leads to heterogeneous distribution of pore network characteristics (pore size and morphology, porosity) through the granular matrix channels. Finally, the presence of macro-pores and cracks results respectively from the difficulty to fill completely the inter-tow porosity and the drying of the SiC matrix after slurry casting step.

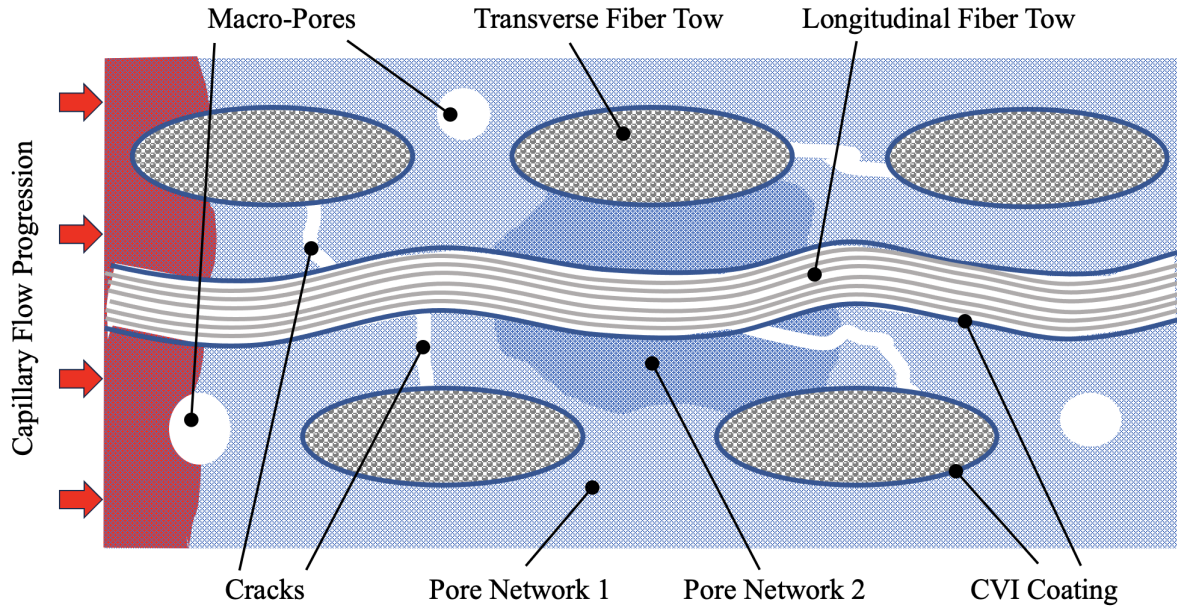


Figure 6.1 Schematic of the typical CMC microstructure that is subjected to capillary imbibition at the melt infiltration step. The following features were simulated in the different experimental phases of this research project to study their effect on capillary flow: heterogeneous pore network, varying channel cross section area, macro-pores, cracks.

The aim of the experiments carried out in this research was to study the effect of various morphological and pore network characteristics on the capillary imbibition. Because the capillary fluid is mainly infiltrated in the granular matrix of the composites, only the SiC matrix was considered in the experiments. The experimental plan was divided in different phases having for objective to isolate separately different microstructural features to study their effect on capillary flow. The experimental results of each phase were presented in Chapter 5. In the present chapter, an effort is deployed to reinterpret these results in order to identify a hierarchy in the ranking of capillary flow mechanisms for better understanding what could occur in the context of melt infiltration of real CMC microstructures containing all the typical features described above. For practical reasons, this research was concentrated on the physical capillary phenomena instead of the possible chemical reactions occurring at high temperature. Therefore, the experiments were carried out with model wetting fluids at room temperature.

6.2 Effect of pore network characteristics on capillary imbibition

The analysis of capillary imbibition within a porous SiC matrix provides valuable insights into several important parameters related to the pore network characteristics, such as the median pore size (d_{50}), the porosity (ε) level and the tortuosity (τ). In order to evaluate

the effect of these significant parameters on capillary imbibition, three formulation types of granular SiC matrix (A, B, and C) were developed in phase I. All these bar-shaped specimens had a thickness of 6 mm.

After completing capillary imbibition tests on these SiC porous specimens with hexadecane and *exo*-DCPD as wetting fluids, the first important observation was that flow behavior of the fluid follows the diffusive type of law (Washburn) where the square of the mass of infiltrated fluid increases linearly with time of imbibition. This was verified experimentally (Figure 5.5) and by numerical simulation using FlexPDE (Figure 5.8). To obtain a good fit of the numerically simulated results with respect to the experimental ones, it was necessary to adjust the value of tortuosity τ characterizing each pore network formulations.

The kinetics of capillary imbibition can be characterized by the slope of the linear $m^2(t)$ relation. From the value of this slope, it is possible to define the effective diameter d_{eff} (Equation 4.1) that corresponds to the diameter of a single capillary tube that would give the same capillary imbibition rate as the one of the porous media. The value of d_{eff} has no real physical meaning in terms of the microstructural metrics of the pore network. Nevertheless, it gives an indication of the overall effect of these parameters on the kinetics of capillary flow. The values of d_{eff} for the three porous SiC formulations of phase I are given in Table 6.1. The largest d_{eff} value gives the fastest kinetic.

Specimen	d_{eff} (nm)	ε (%)	d_{50} (nm)	τ (-)	K (nm ²)
6A	115	48	409	2.8	896
6B	156	50	434	2.3	1 280
6C	107	40	474	3.3	851

Table 6.1 Pore network parameters influencing the capillary imbibition kinetics.

The imbibition rates, as described by the effective diameter d_{eff} , is highly dependent on the structure of interconnected pores in the granular SiC matrix. The most important parameters conditioning the imbibition dynamics are the median pore size d_{50} , the porosity level ε and the tortuosity τ ; these values for each pore network formulation are given in Table 6.1. For the capillary fluid flow to occur, it should be favored energetically by the capillary pressure (inversely proportional to d_{50}) acting as the driving force, and kinetically by lowering the flow viscous resistance.

The decrease of d_{50} lead to an increase of capillary pressure but also an increase of the flow resistance. The impact of tortuosity on capillary pressure is negligible, however it significantly influences the viscous resistance experienced during fluid imbibition. The impact of porosity level on flow diffusivity is not straightforward, since it influences both the hydraulic

conductivity and volumetric capacity of the porous medium in a similar manner (Diffusivity = Conductivity / Capacity). Since all these parameters influence the kinetics of capillary flow, the findings in Section 5.1 suggest their combination into the permeability index K that could be defined by Equation 6.1 [43], which is another representation of Equation 2.22. The evaluation of K for each porous medium formulation is also given in Table 6.1.

$$K = \frac{\varepsilon d_{50}^2}{32\tau} \quad (6.1)$$

It appeared from Table 6.1 that the d_{eff} values rank in the same order than the permeability K . The capillary imbibition rate was clearly higher for SiC formulation of type B, while similar for formulations A and C (with slightly higher rate for A). So in order to design a granular formulation to favor the capillary flow, it would be preferable to maximize the porosity level (up to acceptable range of values) while minimizing the tortuosity by selecting a SiC powder with a narrow particle size distribution. The design criteria for d_{50} is less obvious since this parameter acts inversely on the driving force and on the capillary flow resistance. However, for a given type of SiC particle, the pore size variation stays quite small from one batch to another.

These arguments to explain the effect of pore network characteristics stay valid to describe the results obtained in phase II. In this phase of experiments, the goal was to verify if there was a *specimen size* effect on the capillary imbibition. The results presented in Section 5.2 reveal that the effect of thickness is in fact related to the microstructure of the porous materials that is different between the surface and center of thick specimens. The different microstructures would then result from the heat treatment at high temperature to consolidate the granular materials that is perceived differently from the surface to the center of the specimens. The material at the surface seeing higher temperature has a d_{50} slightly larger than the materials far from the surface. From the opinion of our industrial partner, this effect of heat treatment is certainly exacerbated for the granular specimens fabricated for this research compared to the real SiC/SiC CMC. The homogenization of temperature in the bulk CMC specimens during heat treatment would be favored since the heat conductivity of SiC fibers could transfer the heat more efficiently through the volume of the part. The experimental results on specimens of various thicknesses validated again the diffusive law for capillary imbibition kinetics. The simulation of capillary flow with FlexPDE by inserting gradient of median pore size through the thickness could permit to obtain, similarly to what was obtained experimentally, a parabolic profile for the flow front in the volume of the part. In summary, the results of experiments in phase II could essentially be explained by the effect of pore network characteristics as the ones obtained in phase I.

6.3 Capillary imbibition in diverging/converging cross-section area

The attainment of convergent and divergent cross-sectional morphology is facilitated by the incorporation of geometric modifications that effectively divide the imbibition process into smaller-scale flows in two different branches related to the P shape geometry defined for phase III (Figure 5.29). Here the effective cross section area at the base of the P shape specimen, where fluid infiltration occurs, exhibits a transition zone located at the point of entry of the P loop (Figure 6.2). This transition zone is characterized by a diverging flow corresponding to a momentarily increase of the flow section area. After that, the flow is partitioned into the two branches of the loop. If the cross-sectional area of each branch is locally reduced, causing converging flow, the total area of the two branches is still larger than that of the P leg (15 mm width compared to 12 mm width). The imbibition rate experiences a slight alteration as the fluid traverses the transition zone, primarily because the cross-sectional area available for infiltration increases.

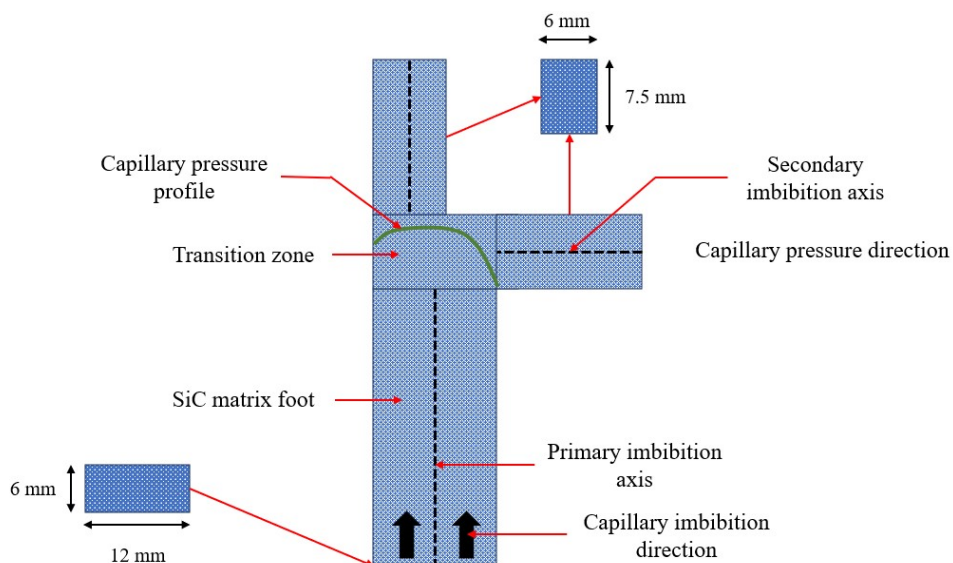


Figure 6.2 Different identified zones in homogeneous P shape geometry that includes the difference in the cross section for the capillary imbibition in the P leg and in the two branches of the P loop.

The experimental results of hexadecane imbibition in the homogeneous P shape specimens reveals a typical diffusive law (Washburn) characterized by a linear relation between the square of the impregnated mass as a function of imbibition time (Figure 5.31). The kinetics differ from the pure straight line of $m^2(t)$ diffusion law only by the appearance of a slight break at a time corresponding to the entry of the flow front in the transition zone.

The numerical simulation of capillary imbibition in a homogeneous P shape specimen reveals

also a noticeable alteration in the rate of imbibition when the fluid crosses the transition zone and experiences flow separation (Figures 5.34 and 5.35). The observed phenomenon can be ascribed to the alteration in the effective cross-sectional area between the base of the SiC granular P shape specimen and the entry in the P loop. The fact that similar trends were obtained for experimental and numerical capillary imbibition kinetics illustrates that the break in the mass impregnated vs time curves is not due to heterogeneity of pore network from one part of the specimen to the other.

The observed transition to a diverging sectional area, which leads to a slightly increased imbibition rate compared to the initial rate, can be attributed to the reduction in the ratio of contact length of the fluid flow front with the contour of the specimen with its total section area. The line of contact could create a certain amount of friction that would slow down the capillary imbibition rate. In the center of the flow front, far from the edges, the effect of friction is less important permitting slightly faster imbibition kinetics.

As mentioned in Section 5.3.1, for the P shape specimens designed for phase III, it was not possible to observe the formation of *dry zones*, neither in experimental results nor numerical simulation of capillary imbibition. This is certainly due to the practical limitations in specimen fabrication leading to section area ratio between different zones too small to cause such phenomenon. This research is unfortunately inconclusive on this aspect but the confidence gained in the use of the simulation tool FlexPDE could be exploited in the future to design more appropriate specimen geometries for better studying this phenomenon.

6.4 Capillary imbibition in heterogeneous porous granular matrix

The production of SiC/SiC CMC by slurry cast process could lead to the formation of granular matrices with various characteristics from one point to another due to non-uniform slurry flow through the fiber preform, the drying conditions or the heat treatment at high temperature prior to the melt infiltration step. The typical CMC microstructure shown in Figure 6.1 illustrates some porous media with different characteristics separated by permeable interface permitting the flow of capillary fluid. The random orientation of the interfaces with respect to the main capillary fluid flow direction could generate some capillary imbibition features that could lead to incomplete imbibition in certain zones of the CMC matrix.

The heterogeneous configurations studied in this research comprise two distinct arrangements that are characterized by the direction of the main fluid flow axis with respect to the interface separating the two porous media. The P shape specimens which exhibits heterogeneity (phase III), serves as the fundamental framework for comprehending the dynamics of imbibition that occur in a direction perpendicular to the interface. The bi-laminar specimens of phase IV

possess interface parallel to the imbibition direction. There exists a fundamental distinction in the mechanism of imbibition between the two arrangements schematized in Figure 6.3.

In the perpendicular arrangement, the capillary fluid flow crosses the interface to pass from one porous medium to the other. This passage lasts only a moment in the course of capillary imbibition experiments. In the bi-laminar arrangement, in addition to the flow parallel to the interface, the transverse flow through the interface is also possible since the interface is permeable to permit inter-diffusion in both transverse directions. For bi-laminar specimens, this longitudinal and transverse dual-flow is present for all the duration of capillary imbibition experiments. The presence of an interface between two porous media with different characteristics would result in a discernible difference in the rates of imbibition on both sides and through the interface.

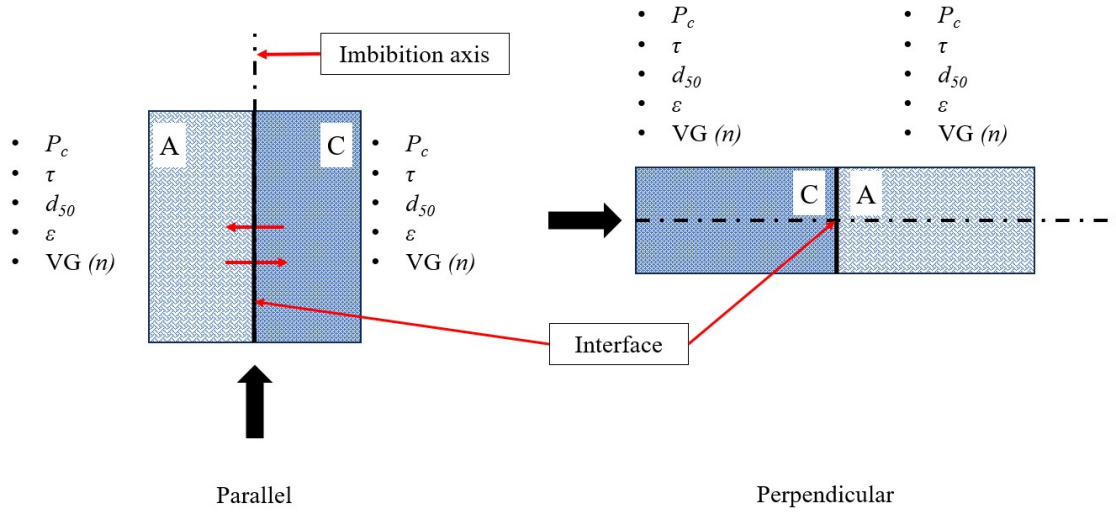


Figure 6.3 Two primary focus configurations for capillary imbibition through SiC matrix with heterogeneous pore microstructure.

The alteration in microstructural characteristics on neighbouring media results in a modification of the imbibition dynamics around the interface. The presence of distinct microstructures gives rise to disparate capillary pressures, leading to varying rates of imbibition in accordance with each respective poral network.

6.4.1 Flow perpendicular to the interface

The capillary imbibition process in the perpendicular configuration of two distinct microstructures results in varying capillary forces, leading to a modification in the imbibition dynamics at the interface of the microstructures. As the fluid moves perpendicularly towards the interface, the capillary pressure undergoes a change. This change is a result of the varying pore morphology as the median pore size changes.

Consequently, the imbibition rate beyond the interface is also affected. The magnitude of this change may vary, either increasing or decreasing, depending on the relative capillary pressure exerted on both sides of the interface. The alteration in the morphology at the interface would result in a certain level of preferential imbibition caused by the capillary pressure difference between the two microstructures.

The experiments that were conducted in phase III with the P shape specimens are not really appropriate because the flow direction in the horizontal branch at the bottom of the P loop is not exactly perpendicular to the interface between the two media. For that reason, the discussion in the present section will be based on the simulation of capillary flow in a simple bar-shaped specimen consisting of two porous media separated by an interface perpendicular to the length of the bar.

For the simulation, the porous media of types B and C were chosen since they have shown maximum and minimum capillary imbibition kinetics respectively. The selected properties of formulations B and C for the simulation were the same as those used in Section 5.3.2. Two different cases were simulated. In the first one, the capillary fluid enters from the bottom in the B formulation and rise towards the C formulation at the other end of the bar. This configuration is named $B \rightarrow C$. Simulations for the second case with capillary fluid going from C formulation to B were named $C \rightarrow B$.

In the first configuration $B \rightarrow C$, the fluid flow kinetics is faster in the B formulation primarily because the permeability of this porous network is higher. As we seen in Section 6.2, the permeability depends on the median pore size, the porosity and the tortuosity. However, if we compare the capillary pressure on both sides of the interface between B and C, the (negative) capillary pressure should be higher on the C side because the d_{50} is smaller for C than for B. Then, when the capillary flow reach the interface, from B towards C, we should expect an acceleration of the capillary imbibition kinetics because the higher suction capillary pressure on side C pulls on the fluid.

The results of the simulation for this case are shown in Figure 6.4 where the distribution of pressure and saturation level are illustrated for different imbibition times corresponding to

the passage of the flow front through the interface. The interface between the formulations B and C is located at mid-length of the bar specimen. The capillary fluid enters the bar from the bottom in the type B formulation. If we consider that the position of the flow front seen from the surface (SFF) corresponds to the saturation level of 50 %, it takes between 1500 and 1800 s for the flow front to cross the interface. The images on the left of Figure 6.4 show the distribution of saturation level at 1300, 1500 and 1800 s. The graphs on the right show the evolution of pressure and saturation along the dotted white line (images on the left), from positions 1 to 3, that crosses perpendicularly the interface.

In terms of pressure, there is a discontinuity of the slope at the interface, even if the capillary pressure increases continuously from the B side towards the C side. However, in terms of saturation level, we see clearly, in Figure 6.4-c for $t = 1800$ s, that there is a drop in the saturation on the B side close to the interface and a sudden increase on the C side. This drop and peak phenomenon tends to disappear with time when the flow front continues towards the C end of the bar. For a short period of time, the higher suction capillary pressure on the C side pulls the fluid from the B side causing a depletion of liquid behind the interface on the B side. This same phenomenon was also observed in Figure 5.43 for the P(AC) configuration of phase III. We see clearly on this last Figure that at the bottom corner of the P loop, the saturation level on the C side is higher than that on the A side.

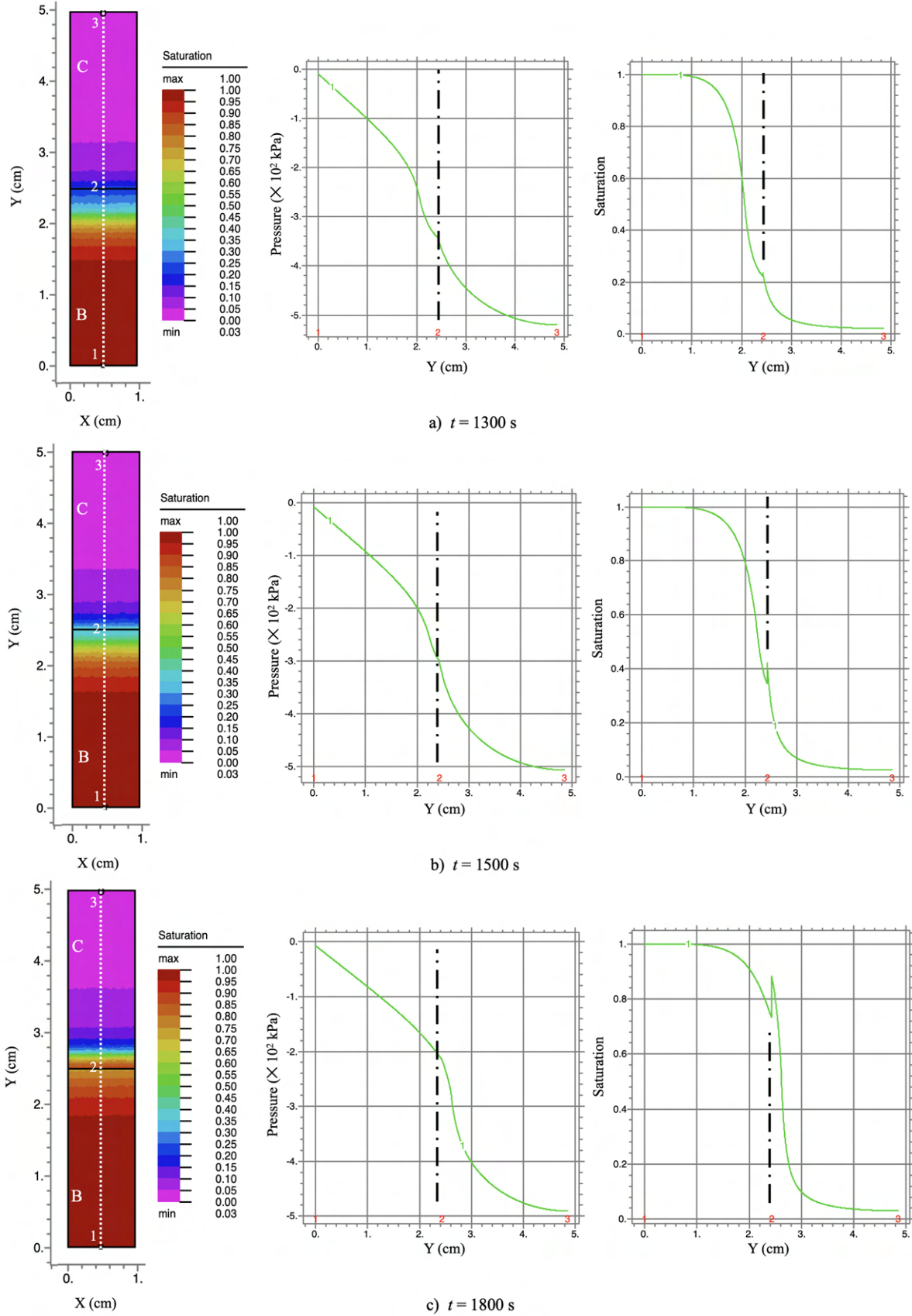


Figure 6.4 Distribution of saturation and pressure along a line perpendicular to the interface for imbibition times of a) 1300 s, b) 1500 s and c) 1800 s.

In the illustration of capillary flow kinetics through the $m^2(t)$ Washburn diffusive law, as it was observed in the simulation of capillary imbibition of P(AC) specimen in phase III (Figure 5.44), the passage from B to C in $B \rightarrow C$ simulation led to an acceleration of the imbibition rate as shown in Figure 6.5. The increase of the slope corresponds to the moment the flow front crosses the interface.

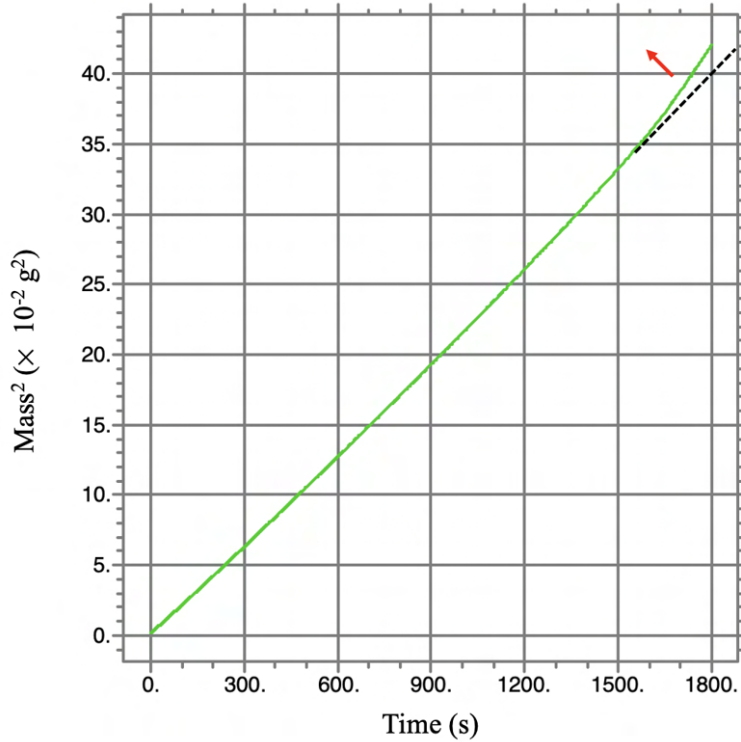


Figure 6.5 Evolution of $m^2(t)$ for $B \rightarrow C$ simulation.

For the second case of simulation, all the parameters were kept constant except for the configuration of the specimen that corresponds now to $C \rightarrow B$. In this case, the capillary flow enters the specimen in the formulation C which has a slower imbibition kinetics than the formulation B at the other side of the interface. This explains why it takes more time for the flow front of the capillary fluid to reach the interface. The results from the simulation of this case are shown in Figure 6.6.

On contrary to what was observed in the previous $B \rightarrow C$ case, what is expected for $C \rightarrow B$ case is a deceleration of the capillary imbibition kinetics when the flow front crosses the interface, since the fluid enters a porous media generating lower capillary pressure. The images on the left of Figure 6.6 show retardation of capillary flow to traverse the interface until the saturation gradient becomes high enough to create sufficient driving force to cross the interface.

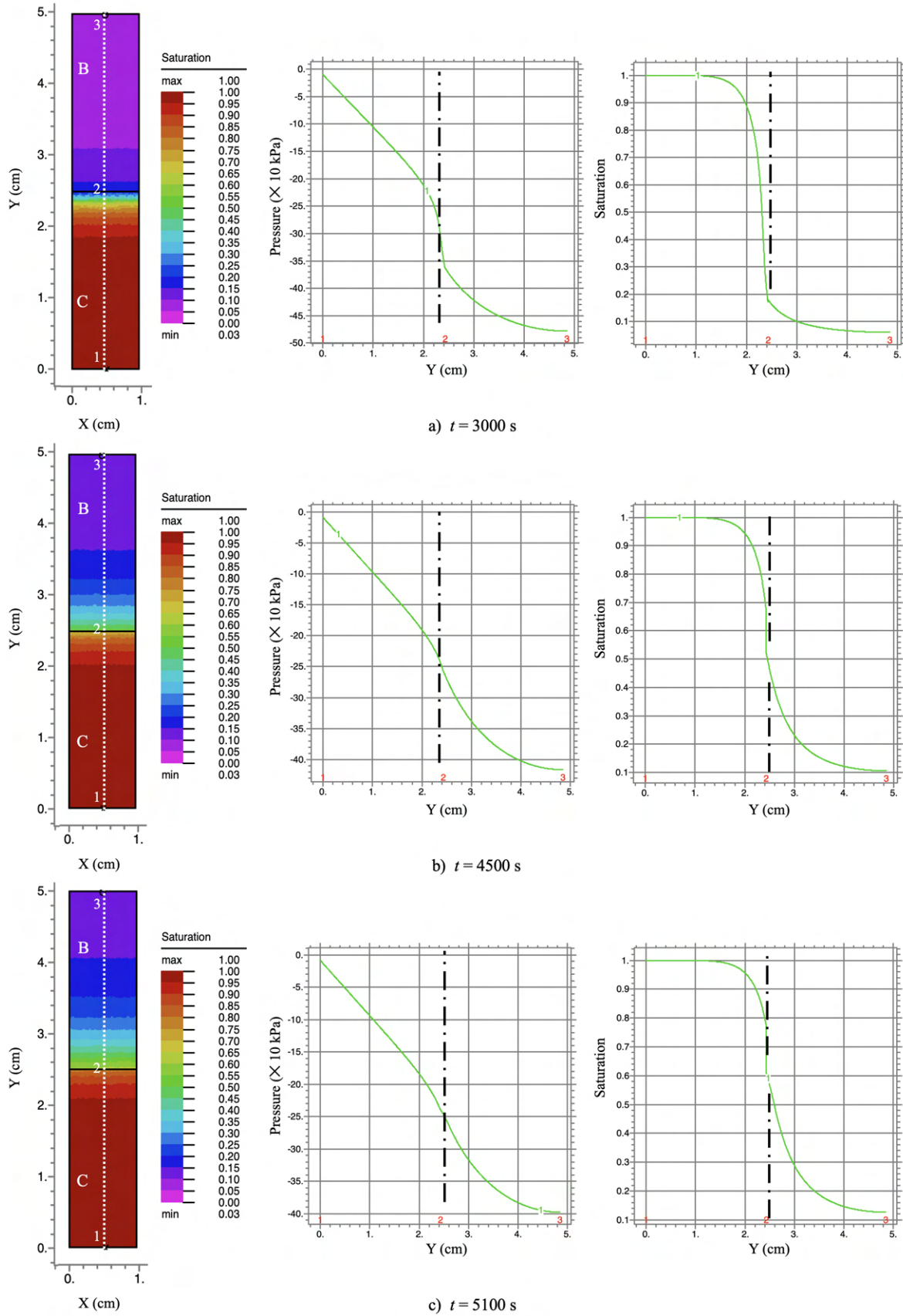


Figure 6.6 Distribution of saturation and pressure along a line perpendicular to the interface for imbibition times of a) 3000 s, b) 4500 s and c) 5100 s.

There is no depletion of liquid behind the interface in this case. In terms of pressure, the gradient seems maximum at about 3000 s; it tends to attenuate at the interface after the passage of the flow front. In terms of saturation around the interface, the gradient is steep but no reversion is observed to create a depletion of liquid on the C side behind the interface.

Again, the capillary flow kinetics represented by the $m^2(t)$ Washburn diffusive law for $C \rightarrow B$ simulation shows the same trend as that was observed in the simulation of capillary imbibition of P(CA) specimen in phase III (Figure 5.44). Figure 6.7 for the simulation of $C \rightarrow B$ gives a deceleration of the imbibition rate when the fluid moves from a medium having larger capillary pressure (C) to a medium having lower capillary pressure (B). The decrease of the slope begins at the moment the flow front arrives to the interface.

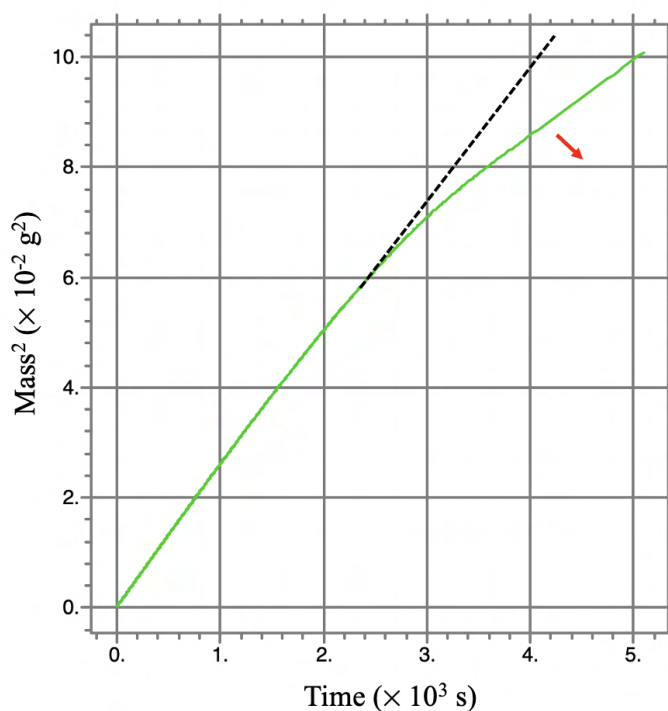


Figure 6.7 Evolution of $m^2(t)$ for $C \rightarrow B$ simulation.

6.4.2 Flow parallel to the interface

For the study of the capillary flow in a direction parallel to an interface separating two different porous media, the definition of bi-laminar specimens as developed in phase IV corresponds exactly to the need of heterogeneous configuration. As for the presentation of capillary flow perpendicular to the interface in Section 6.4.1, the bi-laminar specimen BL(BC) was selected for the analysis of parallel flow because formulations B and C are more distant in terms of their respective permeability.

The capillary imbibition dynamics exhibit variability when adjacent microstructures are present, and the main direction of imbibition aligns with the longitudinal axis of the bi-laminar specimens. The capillary pressure exhibits an elevated value on the C side because the median pore size is reduced compared to that on the B side. However, since the porous medium associated with type C is displaying the lowest porosity and highest tortuosity, this microstructure demonstrates the highest level of viscous dissipation, leading to the lowest imbibition rates.

In the context of neighbouring microstructures exhibiting distinct morphological characteristics, a combined response is observed due to the impregnation of capillary fluid in the adjacent media of the bi-laminar specimens. The interface serves as a mechanism to mitigate the disparity in saturation levels between the flow front on both sides. The phenomenon of transverse imbibition appears to be the primary factor contributing to this behaviour, as it leads to the equalization of capillary pressure at the meniscus with increasing volume of imbibed liquid.

The results for the simulation of capillary flow in bi-laminar specimens of formulations BC are shown in Figure 6.8. On the images to the left, we see that the three imbibition times selected correspond to the position of the flow front before the mid-height, at the mid-height and after the mid-height, which is about 2.5 cm of the bottom of the bi-laminar specimen where the capillary fluid enters the porous materials. As the flow front progresses, the initial step in the saturation level at the interface tends to reduce in intensity. The most interesting feature concerns the evolution of pressure through the interface. Normally, the (negative) capillary pressure increases from the left (B side) to the right (C side). This trend is normal since the d_{50} on the C side is smaller than that on the B side. However, when the flow front reach the dotted white line (images on the left) where the pressure profile is calculated numerically, this corresponding to $t = 2190$ s, we see a strong reversion of this tendency.

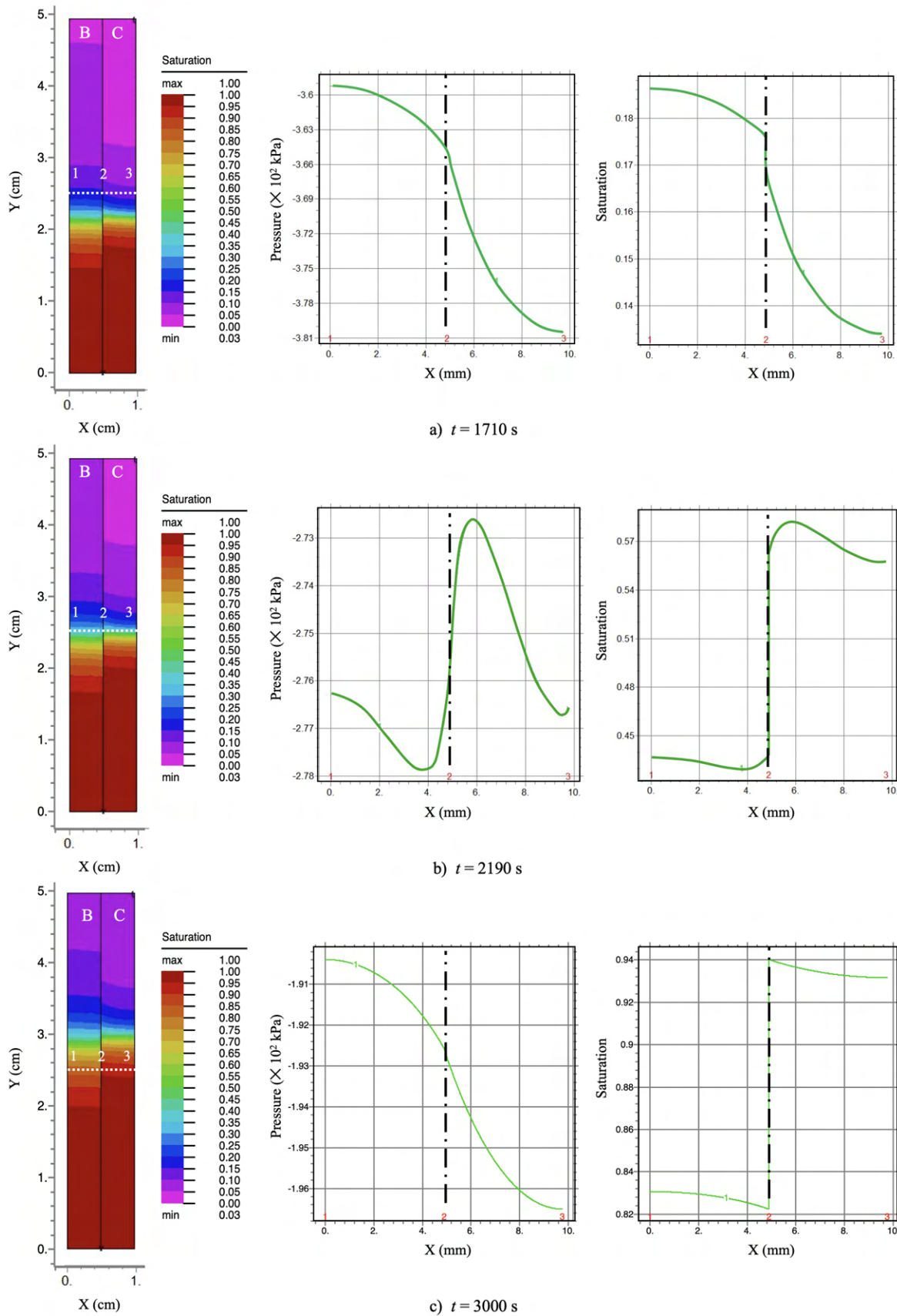


Figure 6.8 Distribution of saturation and pressure along a line perpendicular to the interface for imbibition times of a) 1710 s, b) 2190 s and c) 3000 s.

On contrary to what is occurring in the capillary rise experiments in the case of flow direction perpendicular to the interface between the two different porous media, the capillary rise starts simultaneously on both sides in specimens oriented for parallel flow direction with respect to the interface. At the very beginning, the capillary imbibition kinetics is faster in B formulation than that in C formulation. The principal reason for that was explained in Section 6.2 and is related to the higher permeability of formulation B that leads to lower flow resistance due to viscous loss.

However, the driving force (capillary pressure) is stronger on the C side. When the capillary rise progresses, we observed experimentally that the flow front advances further on the C side than on the B side. This was also confirmed by the numerical simulation with FlexPDE. This phenomenon can be explained by the transverse flow, perpendicular to the interface, from the B side to the C side. The higher suction pressure on the C side then act directly on the interface to pull the liquid from the B side where the fluid flow meet less resistance. It then could be inferred that the C side, especially close to the permeable interface between the two porous media, is mainly filled by the fluid by transverse flow through the interface. It makes sense physically that the fluid follow the easiest path through the porous material structure.

6.5 Capillary imbibition around macropores and cracks

At the beginning of the research project with our industrial partner (Safran Ceramics), in addition to the parameters presented in the phases I to IV, it was decided to characterize the behavior of capillary flow in granular porous SiC containing macro defects such as those illustrated in Figure 6.1. This experimental task was carried out in the context of master thesis work of Floriane Dewart [140] who developed the experimental approach and the analysis of the results of phase V on the effect of macro defects on capillary flow. The results of this work were not presented in the present thesis but it is interesting now to describe the main results to situate the hierarchical effect of these results with respect to those characterized in phases I to IV.

Two types of defects were simulated in phase V. The first one consisted in macro pores having diameters in the order of 100 μm . The volume fraction of these macro pores was set between 2 and 5 %. The second type of defect was a planar void to simulate the presence of a crack. The planar defects had the following dimensions: 76 μm thickness, 600 μm width. The length of the planar defect could go through the dimension of the specimens or not. The details of the fabrication of specimens by slurry cast method are described in the thesis of F. Dewart [140]. It could be said that the macro defects were produced by introducing in the

liquid slurry sacrificial polymer spheres (macro pores) and ribbon (planar crack) that were eliminated during the heat treatment step after slurry cast but before capillary infiltration.

The existence of granular imperfections, regardless of their form or severity (planar and spherical voids), has a negative impact on the overall performance of the matrix. The diverse flaws have been previously examined, alongside their consequences on the efficacy of high-temperature ceramics. However, it is important to note in terms of capillarity phenomenon that there exists a disparity in scale between the macro voids and the poral network porosity.

In the presence of spherical macro pores, as depicted in Figure 6.9, it becomes evident that the flow front progresses unhindered, devoid of any discernible alteration in its morphology. In the example shown in Figure 6.9, the progression of fluid manifests as a parabolic front, which subsequently halts upon encountering the interface layer of bi-laminar specimen. The work of Dewart [140] shows that capillary flow kinetics, characterized by $m^2(t)$ curves, was not altered by the presence of macro pores. This could be due mainly to the low volume fraction of macro pores in the specimens.

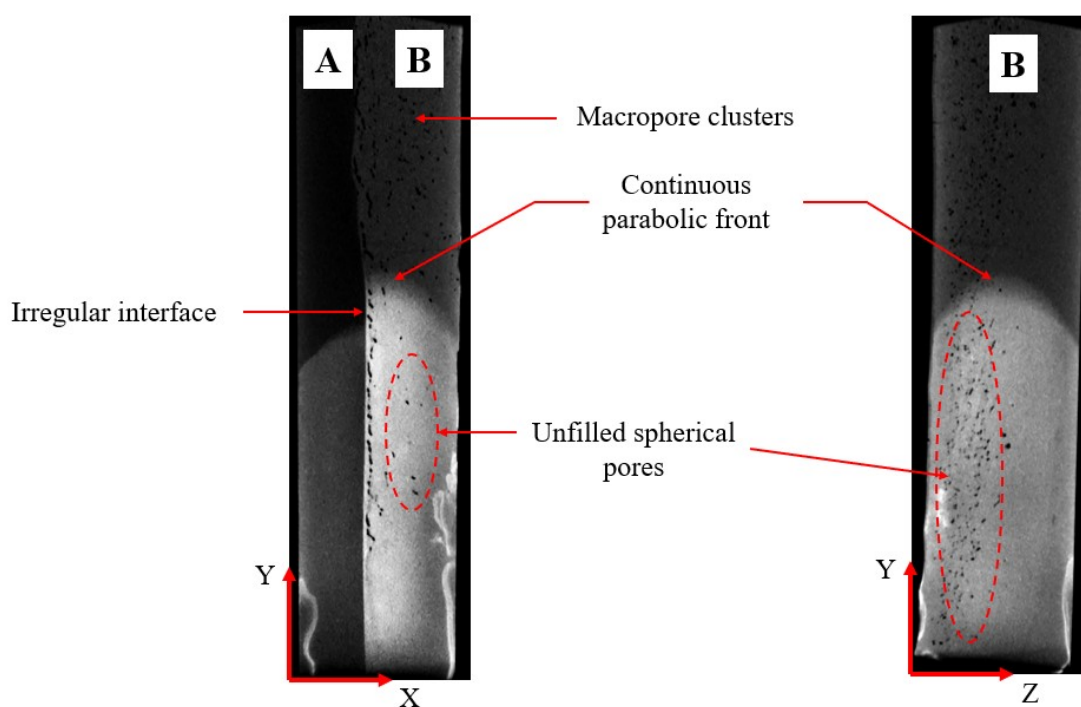


Figure 6.9 X-ray tomography images of capillary imbibition dynamics with continuous parabolic front generation in bi-laminar specimen AC containing macro pores.

The presence of clustered spherical unfilled macro pores in close proximity to the interface layer suggests that the negative capillary pressure generated by the macro pore itself is

inadequate to generate capillary flow to fill the spherical voids. Part of the reason explaining the non-filling of the macro pores is related to the relative capillary pressure on both sides of the interface delimiting the contour of the macro pore.

Figure 6.10 illustrates that in the granular matrix surrounding the macro pore, the capillary pressure is conditioned by the d_{50} value characterizing the porous media, which is in the order of 300–400 nm. The macro pore considered in this study had a diameter d_{pore} in the order of 100 μm , which is about three orders of magnitude larger than the micro porosity of the granular media. The driving force for filling the macro pore is then negligibly small. As a consequence, the capillary fluid fills the porous media around the macro pore, leaving the macro pore cavity empty. It suggests that spherical voids above a specific critical diameter have minimal impact on the dynamics of imbibition.

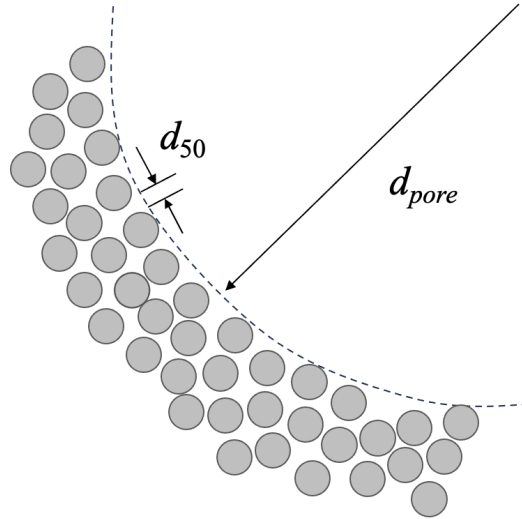


Figure 6.10 Relative dimensions of the median pore size of the granular matrix (d_{50}) and that of the macro pore (d_{pore}).

The fluid dynamics in the presence of transverse cracks, as opposed to a uniform granular matrix, have been illustrated in Figure 6.11. It clearly demonstrates the preferential advancement of the fluid around the boundaries of the cracks, rather than initially filling the cracks. This observation is significant as it supports the dominance of preferential capillary-induced imbibition of the granular matrix over macroscopic planar defects. Again the large size of the crack with respect to the d_{50} of the surrounding granular matrix does not generate capillary pressure large enough to favor the filling of the crack cavity.

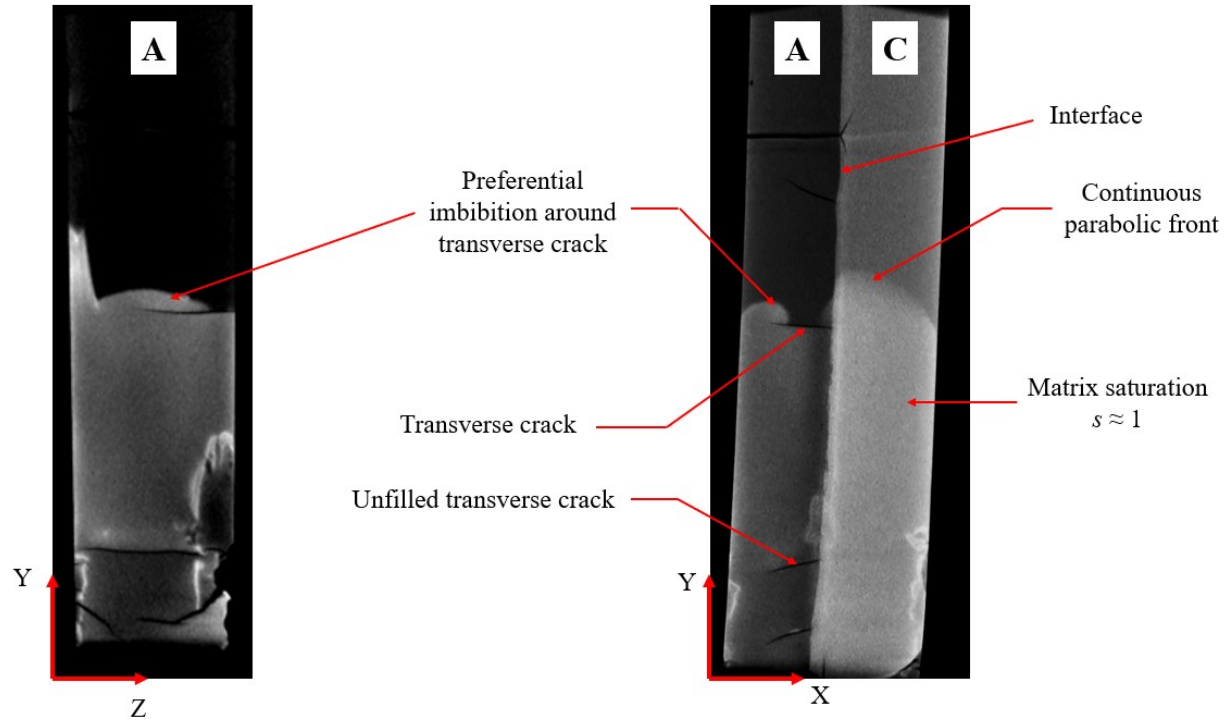


Figure 6.11 X-ray tomography images of the evolution of volume flow front for the two layers of a bi-laminar specimen with presence of transverse crack that disrupt the imbibition.

When longitudinal cracks are present within the volume of a granular porous specimen, we observe the formation of voids spanning the entire length of said cracks, as shown in Figure 6.12. This observation demonstrates that even in the presence of full saturation in the surrounding granular matrix, the capillary pressure generated by the size of the crack fails to exert sufficient force to drive the fluid into the crack, regardless of its alignment in relation to the direction of imbibition.

Despite the discernible discrepancy in capillary pressure existing between the two distinct microstructures of the bi-laminar specimen of Figure 6.12, the phenomenon of fluid migration from one layer to another remains absent. Conversely, the process of infiltration occurs along the prominent boundaries of the distinct interface layers, devoid of any ingress of fluid. In this case of bi-laminar BC specimen, this explains why the imbibition kinetics is fastest on the B side than that on the C side, because the absence of transverse flow makes the B and C layers to act independently.

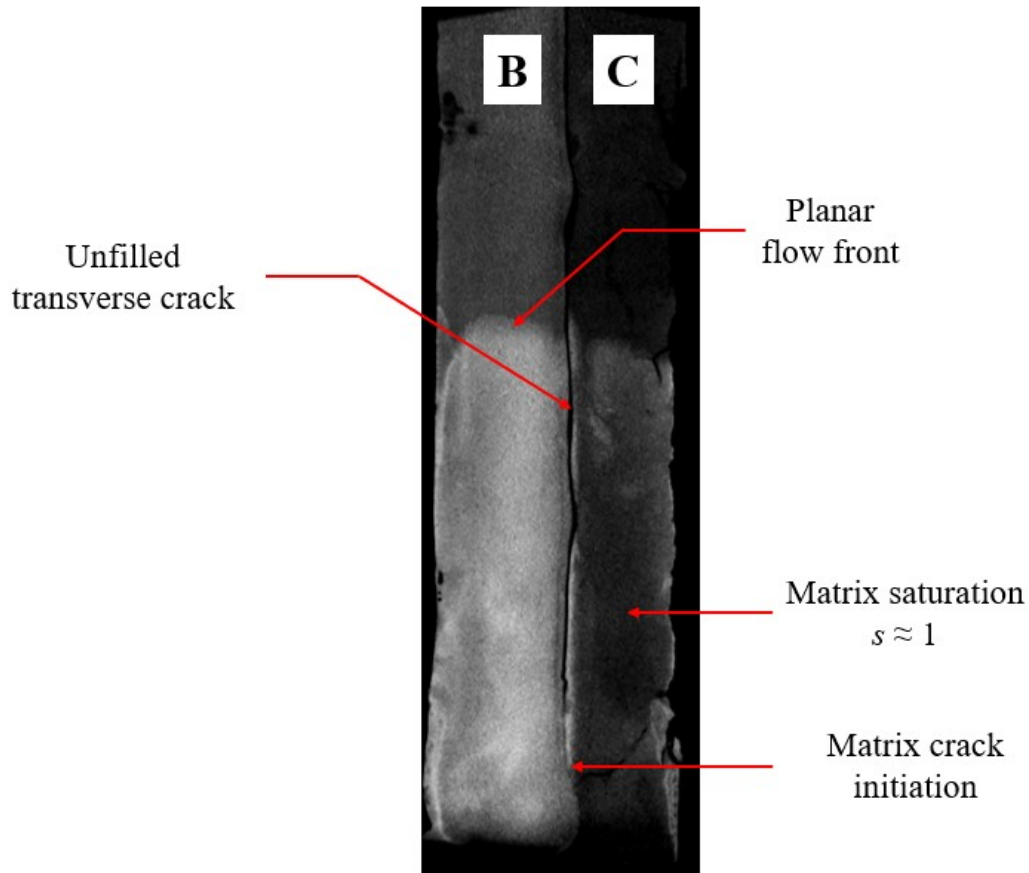


Figure 6.12 Location of longitudinal crack at the interface of bi-laminar specimen which remains unfilled, even with fluid progression in porous media on both sides of the interface.

Another phenomenon that was observed by Dewart [140] (Figure 6.13) and that could be seen in Figure 6.12 for longitudinal crack is the apparent higher concentration of the fluid (higher intensity on X-ray tomography, Figures 6.12 and 6.13) on the planar surfaces of the crack. It seems that the roughness of the granular matrix at the crack surfaces could generate capillary pressure by itself, favoring the surface fluid flow. The wetting of rough surfaces was discussed briefly in Section 2.5.3.

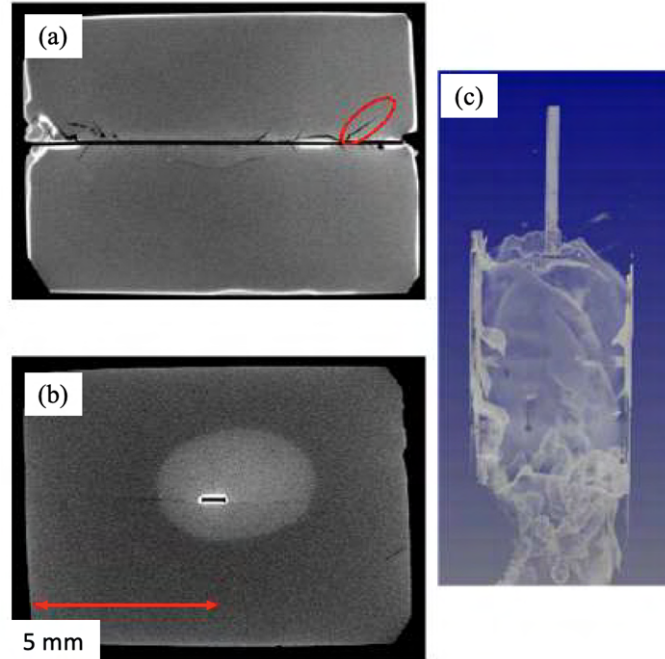


Figure 6.13 X-ray tomography images of planar defects simulating cracks. a) Unfilled longitudinal planar defect going through a granular SiC specimen. b) Planar defect seen from its extremity. c) 3D images of *exo*-DCPD infiltrated specimen with planar defect. The capillary fluid impregnation on the surfaces of the crack extends the flow front in the matrix. From [140].

Finally, it is important to consider that the capillary imbibition experiments that were carried out in this research were done under atmospheric air pressure, preventing then the complete filling of the macro defects introduced in the granular specimens. When the capillary fluid infiltrated in the matrix surrounds the macro defect, the entrapped air further limits the filling of the defect because the internal air pressure opposes that of capillary phenomenon.

When these two pressures reach equilibrium, the cavity cannot be filled anymore. With similar experiments carried out by Hugo Carpentier at LCTS in his Ph.D. thesis [155] on capillary infiltration of liquid silicon at high temperature, he could obtain complete filling of macro pores and cracks because the capillary imbibition experiments were performed under vacuum. In this case, the notion of irreducible porosity does not hold.

Based on these empirical observations, one can infer that the existence of planar matrix cracks poses an obstacle to achieving a homogeneous dispersion of the model fluid during the capillary imbibition process, if the fluid has no path to go around the crack. The presence of spherical pores does not inherently impact the dynamics of imbibition. These mechanisms are schematized in Figure 6.14.

However, it is important to note that excessively large spherical pores can potentially undermine the thermostructural integrity of the CMC. The process of matrix fabrication is a meticulously executed procedure, wherein each processing step is subjected to stringent control measures in order to attain the intended microstructure. This microstructure, in turn, is crucial for manifesting the desired properties that are needed for hot gas sections within of turbine engine.

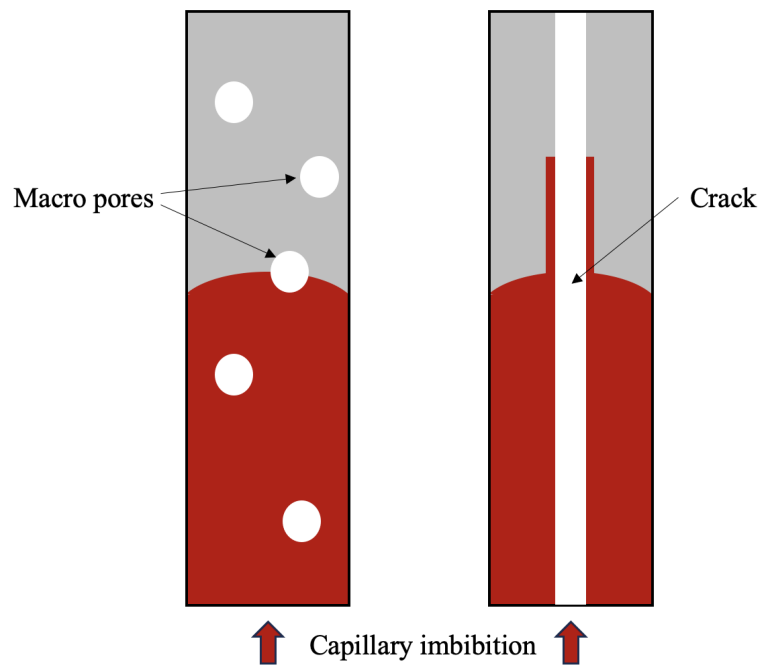


Figure 6.14 Influence of macro pores and cracks on capillary infiltration. If the capillary rise is not disturbed by macro pores, it tends to extend the flow front along the surface of the crack. Inspired from [140].

6.6 Interpretation of FlexPDE simulation

The FlexPDE numerical tool used in this research project solves Richards differential equation that describes the capillary infiltration of unsaturated porous media by fluids. Results of this research show that some predictions by the numerical simulation are in good agreement with the experimental results obtained from capillary rise experiments in porous SiC matrix of various shapes and configurations. The most remarkable experimental result is the capillary imbibition kinetics that could be associated with the Washburn law giving a linear relation between the square of the impregnated mass m^2 with time t . The simulated results with FlexPDE gives the same type of linear $m^2(t)$ response when the pore network properties of the porous media are inserted as entry parameters in the numerical model.

The only parameter that has to be *adjusted* is the tortuosity τ . Even if this parameter is otherwise difficult to characterize experimentally, the values that were obtained for characterizing the different SiC formulations (in the range 2–3) are comparable to those cited in the literature [91]. The adjustment of the tortuosity value for each formulation is done to obtain the same slope for $m^2(t)$ curves. This obviously leads to the same values of d_{eff} measured experimentally and calculated numerically.

The other information provided by the FlexPDE application that is well correlated with the experimental results is the shape and position of the flow front that could be seen on the surface of the specimen during capillary imbibition. The correspondence between the experimental observation and the simulated flow front is obtained if we consider the saturation level of about 50 %. Based on that consideration, the position of the flow front predicted by FlexPDE shows a good agreement in the cases of homogeneous specimens, heterogeneous specimens (phases III and IV) and P shape specimens (phase III).

The only discrepancy between simulation and experiments is the extended saturation gradient resulting from the simulation, while the experiments tend to show abrupt step of the saturation s from $s = 1$ behind the flow front to $s = 0$ above the flow front. Recent results in the context of this research that will be published [145] by Thibault et al. shows that the saturation gradient is effectively abrupt.

This anomaly of the FlexPDE simulation result comes from the diffusive nature of the phenomenon described by Richards equation. This implies that there exists a dependence relationship among saturation, pressure, hydraulic conductivity, and the pore network's capacity. In addition to the aforementioned inconsistencies about the saturation profile inside the porous material, the findings obtained from FlexPDE software offer a reliable representation of the actual conditions, provided that the saturation level corresponding to 50% is utilized

to define the location of the flow front line.

6.6.1 Saturation

The FlexPDE application that is used to simulate the capillary phenomena incorporates the Richards equation, which is a primary saturation-based approach. The degree of saturation is directly dependent on the hydraulic conductivity ($\text{m}^2/\text{Pa}\cdot\text{s}$), which attributes the fluid transfer and the capacity (Pa^{-1}), which is related to the pressure gradient. The material with higher hydraulic conductivity would possess a higher degree of poral permeability, which would facilitate a higher susceptibility to imbibition. Both the conductivity and the capacity are related to the level of fluid saturation in the porous media. To illustrate this phenomenon, we selected the example of heterogeneous specimen BC with an interface separating the two media oriented perpendicularly to the fluid imbibition direction. This is shown in Figure 6.15.

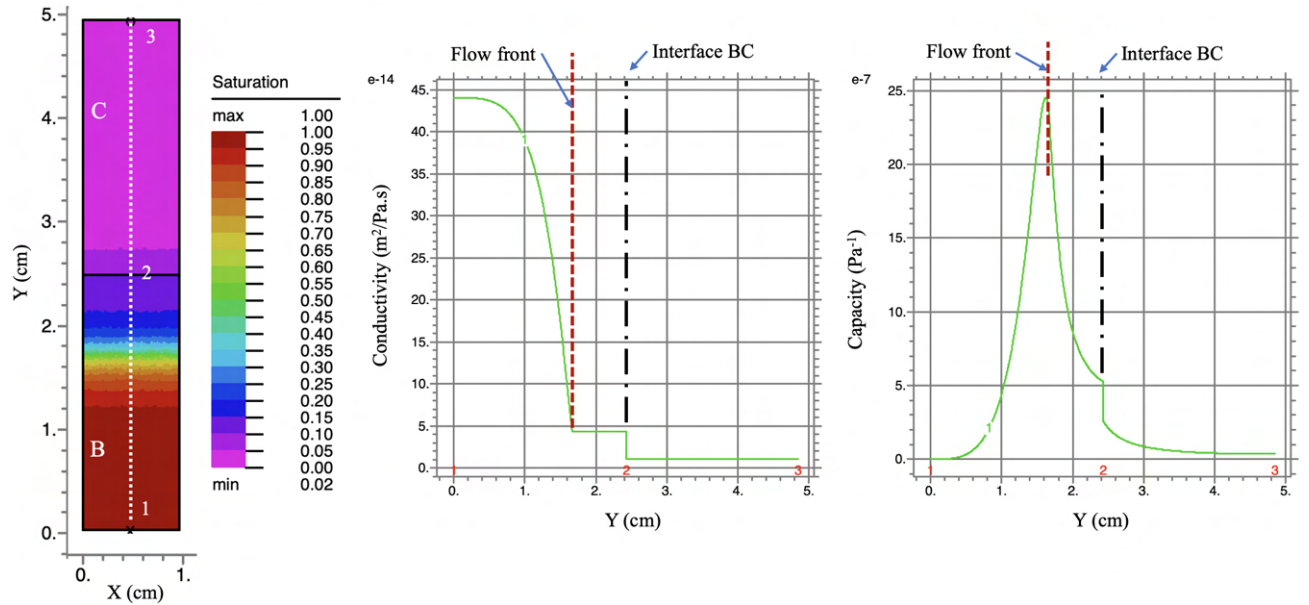


Figure 6.15 Saturation profile for heterogeneous BC specimen with capillary flow perpendicular to the interface. Profiles of conductivity and capacity along a longitudinal line 1-2-3 perpendicular to the interface. $t = 900$ s.

The saturation profile on the left of Figure 6.15 shows that for $t = 900$ s in this configuration of porous specimen, the flow front line is about at 1.6-1.7 cm from the bottom face of specimen, below the interface between B and C formulations located at 2.5 cm. The simulation with FlexPDE predicts a gradient of saturation from 1 to 0 between $Y = 1.2$ and $Y = 2.8$ cm respectively. We see on the graph in the middle that conductivity decreases with the reduction of saturation down to the position of the flow front from where it takes the characteristic

value of the poral network of formulation B, which decreases further above the interface in the poral network of formulation C having lower permeability.

The conductivity then varies with the level of saturation. The same trend is observed for the capacity (graph on the right) where the maximum in capacity corresponds to the position of the flow front. Above and below the flow front, the capacity decreases. The capacity shows also a step at the interface between the two porous media. This simulated behavior is a consequence of imposing a certain gradient of saturation that is mostly related to the Van Genuchten function that is used as a closure relationship between saturation and pressure.

6.6.2 Van Genuchten parameter

To run the numerical simulation with FlexPDE, it is also necessary to insert the n parameter of the Van Genuchten (VG) equation that is associated with the relationship between the saturation s and the pressure through pore size distribution. The VG equation describes the increase of saturation of the porous media with an increase of pressure. The value of the parameter n dictates the rate (or the slope) at which the saturation increases with the pressure. The higher is the value of n , the steeper is the increase of saturation.

To identify the value of n to be inserted in FlexPDE simulation, it is suggested to mimic the experimental result of mercury intrusion porosimetry giving the curve of cumulative infiltrated volume as a function of pressure. The discrepancy between experimental saturation gradient and the one obtained by numerical simulation could be partially explained by the proposed determination of the VG parameters (n and α) from the MIP experimental result. It could also be that maybe VG which gives a unique relation between pressure and saturation is not adapted to model capillary imbibition.

Initially, the VG equation describes a capillary phenomenon while the MIP measure does not come from capillary experiment since it is necessary to push the non-wetting fluid (mercury) to infiltrate the porous sample. For the needs of FlexPDE, in the present research, the value of n was selected for each poral network from the approximate fitting between the MIP curve and the VG equation. This is illustrated in Figure 6.16 for specimens of formulation A, where the value $n = 5$ seems acceptable to obtain a good fit of the slope in the transition between saturation values of 0 and 1.

Even if it is true that VG function increases with pressure as the MIP infiltrated volume, does it have to follow the same rate? In Figure 6.16, we show the shape of the VG function if we impose a value of $n = 10$. In this particular instance, the observed augmentation in saturation exhibits a more sudden change, deviating from the slope of the MIP-infiltrated volume. Nevertheless, it has been shown that this phenomenon leads to an amplified gradient

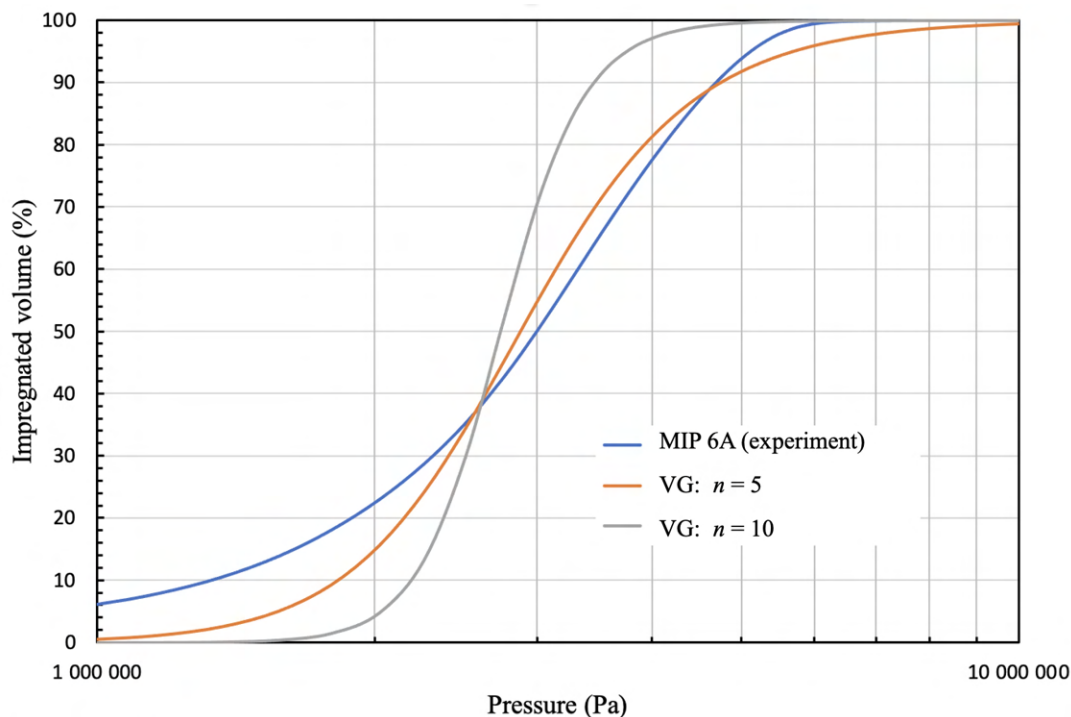


Figure 6.16 Fitting of the experimental MIP curve for formulation 6A with Van Genuchten function for different values of n parameter.

of saturation values within a shorter distance along the imbibition direction, resulting in an accelerated transmission process. The effect of this change for the value of n is illustrated in Figure 6.17 showing the saturation profiles in SiC porous formulation A after 2000 s of hexadecane imbibition. Apart from the value of n , all the other parameters input in FlexPDE were the same. We see that for $n = 10$, the saturation gradient is more pronounced.

The result of the simulations gave similar values of impregnated hexadecane mass in both cases: 604 mg for $n = 5$ and 616 mg for $n = 10$. By selecting an even higher value of n to run the simulation, meaning a steeper saturation gradient, the numerically simulated results in terms of saturation profile would show a better fit with the experimental observations. The issue in this particular situation arises from the numerical challenges encountered while executing the FlexPDE program. These challenges stem from both the sudden discontinuity of the VG function and its derivative, which are utilized to solve the Richards equation.

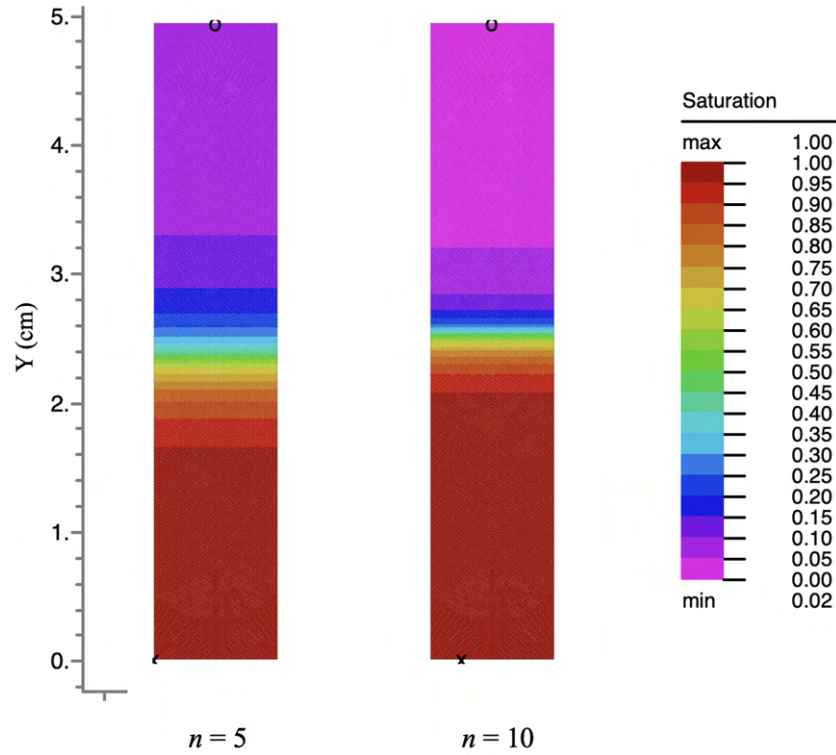


Figure 6.17 Simulation of saturation profiles for 6A formulation. The Van Genuchten parameter n was the only one that was changed between the two simulations. Duration of imbibition: 2000 s.

Again, the discussion about the necessity to fit the MIP experimental results with the VG function to obtain the n parameter is still open. More refinements in the setting of calculations parameters (mesh grid, time step, ...) could be introduced in FlexPDE to better fit the experimental results from capillary imbibition experiments. In this case, new values of tortuosity would be obtained but the ranking of these values with respect to the pore media formulations and their amplitude would probably be similar to those obtained in the present research. However, in spite of this discrepancy related to the saturation profile, it appears that the simulated results coming from FlexPDE are valuable to describe at least qualitatively the trends observed experimentally in the capillary imbibition of porous granular SiC matrix.

CHAPTER 7 CONCLUSION AND FUTURE SCOPE

The primary aim of this study was to get a deeper understanding of the mechanisms underlying capillary-induced imbibition in a silicon carbide (SiC) matrix. A characterization procedure was devised to establish an equivalent correlation between rheological properties of a model fluid at ambient temperature and liquid silicon at high temperature. This approach was adopted due to the difficulties encountered in achieving consistent results and managing resources when conducting characterizations at elevated temperatures. The impact of the interaction between chemical components of the matrix and fluid has been disregarded at ambient temperature in order to provide a more straightforward comparison. The objective of this study was to examine the impact of key parameters such as surface tension, wetting angle, viscosity, and density on the correlation of imbibition dynamics between high temperature and ambient temperature.

The bibliographic analysis encompassed the discernment of the underlying principles governing the capillary phenomenon, which dictates the movement of fluids within a comparable capillary structure. This was subsequently followed by a thorough investigation into its manifestation within a porous SiC matrix. The pertinent analytical methodologies were explicated, accompanied by a comparative analysis of the simulated capillary imbibition using the FlexPDE simulation tool. The introductory segment delved into the methodologies and experimental techniques employed to elucidate the phenomenon of capillary rise in diverse microstructural contexts. The methodologies employed are constrained to conducting experiments under ambient temperature conditions, utilizing model fluids that possess rheological similarity.

In order to achieve these objectives, a comprehensive state of the art was designed that is based on the intricate aerospace-grade components to establish a basis for formulating hypotheses that elucidate the underlying forces interplay of the observed capillary imbibition dynamics that also include morphological anomalies in the capillary phenomena. The significant role of a granular matrix and the complex poral network it possesses has been found. The phenomenon of granular amalgamation that is followed by the enlargement of pores during high temperature heat treatment (THT) has been observed to have a significant impact on the evolution of the final pore network, resulting in varying pore diameters. This process is driven by the minimization of surface energy.

These first analyses enable the validation of the observed capillary imbibition mechanisms on the model materials. The primary mechanism responsible for the filling of micro porosity

inside the granular matrix is the direct contact between the matrix and the liquid reservoir. The permeability of a material is determined by the collective influence of its pore size distribution (characterized by d_{50}), porosity, and tortuosity. These morphological factors work together to affect the flow of fluids through the material. Additionally, this interplay of parameters also influences the different force components that govern capillary imbibition. The advancement of the diffuse flow front occurs when the negative capillary pressure surpasses the dissipation of viscous and inertial forces caused by the pore shape, which is determined by three essential characteristics. A reduction in the median pore size would result in an elevation of the negative capillary pressure, while simultaneously augmenting the viscous dissipation during the process of capillary imbibition in the SiC matrix. A greater permeability would enhance the rate of imbibition; nevertheless, it cannot be regarded as an isolated dominating feature, but rather must be considered in conjunction with other morphological parameters. In order to enhance the consistency of the imbibition process, it is necessary to attain an optimal equilibrium between the driving force and the flow resistance imposed by the porous material.

The key inferences from the second phase of this work indicate a correlation between the thickness of the specimen and the resulting pore size achieved using heat treatment (THT). This manifests as a slight difference in median pore size between the surface and centre as a gradient. The effect of the external matrix surface is a visible retardation of the imbibition, while the central matrix surface does not impede the capillary flow. There is also a radial flow front that is observed in the direction of the pore size gradient that is induced due to the disproportionate effect of THT on the microstructure. In comparison to a matrix with a higher thickness, a finer granular phase exhibits a greater expansion of its pores. The high temperature heat treatment is also responsible for the generation of the requisite microstructure that promotes capillary imbibition.

The minute change in the imbibition rate may be magnified by raising the proportional scale of specimen dimensions by a factor of 1:10. This allows for a more dramatic observation of the effect of the transition zone on capillary imbibition, which is influenced by the variation in cross-sectional area. The imbibition rate has a direct proportionality to the cross-sectional area of the surface that is in contact with the fluid reservoir.

When the capillary imbibition occurs in a heterogeneous porous media, the abrupt alteration in the microstructural composition on both sides of the interface separating the two media induces a sudden modification in the rate of imbibition, contingent upon the transition in hydraulic conductivity that is influenced by the corresponding negative capillary pressure.

When the fluid meniscus penetrates perpendicularly through the interface, the dissimilar-

ity in capillary pressure between the two extremities of the specimen instigates the abrupt aspiration of the fluid meniscus at said interface. The permeability perpendicular to the imbibition direction is influenced by the variation in capillary pressure, porosity, and median pore size. The sudden alteration in saturation levels would result in the occurrence of preferential imbibition towards the microstructure, hence leading to an increase in capillary pressure.

In the context where capillary flow direction is parallel to the interface separating the two media, the presence of an adjacent microstructure induces diverse capillary pressure, thereby altering the conventional behaviour of the fluid meniscus. Specifically, the adjacent capillary pressure serves to enhance the adjacent diffuse front, which is associated with the microstructure possessing higher permeability. This preference is further enhanced by the dominating imbibition direction, which involves a mix of longitudinal diffusion along the imbibition axis and transverse diffusion through the interface between the two neighbouring microstructures.

Different factors have an impact on the imbibition phenomena in presence of macro pores and cracks. In the case of transverse cracks, the filling of the cavity by capillary fluid does not occur, even if the surrounding matrix without cracks tends to be filled preferentially. Despite the occurrence of imbibition parallel to the longitudinal cracks, the filling of those cracks does not occur neither. The imbibition dynamics remain unaffected by the presence of macro pores, as these larger voids do not participate in the imbibition process and are not filled with fluid. Furthermore, the capillary pressure exerted by the macro defects is insufficient to drive the fluid into the cracks and macro pores.

FlexPDE offers a methodology for resolving Richards equation pertaining to an unsaturated porous SiC matrix. Results of the numerical simulations show good qualitative correlation with the experimental observation of Washburn diffusive law of capillary impregnation, characterized by a linear evolution of the square of the impregnated mass of fluid with time. If the placement of the flow front is taken into account at a saturation level of 50 %, the simulation with FlexPDE gives also a good correlation of the flow front behavior in a variety of conditions: diverging/converging flow, flow through heterogeneous porous media, flow around macro defects. The correlation of the observed flow front position with the saturation level of 50 % seems to be due partly to the scheme to determine the Van Genuchten parameter n from the experimental results of mercury intrusion porosimetry. While the simulation tool does have some minor constraints, it offers a straightforward means of forecasting the capillary imbibition dynamics pertaining to the SiC matrix.

Drawing upon the empirical evidence pertaining to capillary imbibition within the SiC matrix, one can posit a series of thoughtful considerations regarding the composition of a ceramic

matrix composite (CMC) wherein the fibrous component assumes a pivotal role within the matrix phase, replete with its inherent complexities. The phenomenon of imbibition would manifest a distinct hierarchical pattern of fluid movement, which is instigated by the coexistence of multiple phases surrounding the consolidated matrix. The phenomenon of preferential imbibition, facilitated by the morphological interaction of the fibrous phase, exhibits noteworthy characteristics. This has been substantiated by the observations made via X-ray tomography.

Future scope

In order to further expound upon the present research endeavour, it may be advantageous to introduce a certain level of intricacy by incorporating a solitary fibre tow within a SiC matrix, positioned in two distinct orientations: parallel and perpendicular to the longitudinal axis of said matrix. The current investigation is confined to the phenomenon of capillary imbibition within the matrix and its associated microstructural irregularities. Nevertheless, the inclusion of fibre would effectively simulate the phenomenon of capillary imbibition within a SiC CMC, which consists of both a matrix and fibre phase. The elucidation of capillary dynamics within a matrix featuring a solitary pore necessitates the integration of the intricate interplay among fibres, pores, and the diffusive flow front. The empirical observations pertaining to this particular scenario would yield a more precise depiction, thereby enhancing our comprehension of the intricate dynamics of capillary imbibition. This knowledge could subsequently be extrapolated and applied to gain insights into the imbibition dynamics under elevated temperatures, specifically within the context of the genuine melt infiltration process employed in the production of advanced ceramic matrix composites.

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