

Expérience et étude numérique sur la dynamique de transfert d'humidité dans les matériaux cimentaires poreux à plusieurs échelles

Xiaoyan Ma

► To cite this version:

Xiaoyan Ma. Expérience et étude numérique sur la dynamique de transfert d'humidité dans les matériaux cimentaires poreux à plusieurs échelles. Génie civil. Université Paris-Saclay, 2020. Français. NNT : 2020UPASN025 . tel-03027190

HAL Id: tel-03027190 https://theses.hal.science/tel-03027190

Submitted on 27 Nov 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Experimental and numerical study on moisture transfer dynamics in multiscale porous cementitious materials

Thèse de doctorat de l'université Paris-Saclay

École doctorale n° 579, Sciences mécaniques et énergétiques, matériaux et géosciences (SMEMaG) Spécialité de doctorat: transfer phenomena and civil engineering Unité de recherche : LMT-UMR: 8535 Référent : Université Paris -Saclay

Thèse présentée et soutenue à Paris-Saclay, le 17/06/2020, par

Xiaoyan MA

Composition du Jury

Patrick PERRE	Drésident	
Professeur, CentraleSupélec	President	
Abdelkarim AÏT-MOKHTAR	Development	
Professeur, Université de La Rochelle	Rapporteur	
Sabine CARE	Dependenteur	
Directrice de recherche, Université Gustave Eiffel	Rapporteur	
Miguel AZENHA	Franciscotoria	
Assistant Professeur, University of Minho	Examinateur	
Rachid BENNACER	Dinastaun da thèsa	
Professeur, ENS Paris-Saclay	Directeur de these	
Farid BENBOUDJEMA		
Professeur, ENS Paris-Saclay	Co-Directeur de thé	
Jean-Luc ADIA	T. 11/	
Ingénieur Chercheur, EDF	Invite	

lhèse de doctorat

NNT : 2020UPASN025

Nothing in life is to be feared, it is only to be understood.

Now is the time to understand more, so that we may fear less.

— Marie Curie (1867 - 1934)



ECOLE DOCTORALE N°579 sciences mécaniques et énergétiques, matériaux et géosciences (SMEMaG)

Title : Experimental and numerical study on moisture transfer dynamics in multiscale porous cementitious materials

Keywords : complex porous material; relative humidity; moisture transferring model; parameters optimization; multi-scale structure

Abstract :

Climate change in the last decades is increasingly influenced by humans activities including the emission of greenhouse gases. In the construction field, cement production contributes to about eight percent of the world's carbon dioxide emissions, due to the fact that concrete is the most widely used manufactured material in existence. Therefore, the sustainability of concrete and the durability of their structures have significant concerns of the global energy consumption and worldwide environmental impact.

Research results showed that the structural behavior of concrete is closely related to the variation of water level in concretes and the loss of free water may induce a modification of its elastic properties, strengths, shrinkage, or creep deformations. Thus, the knowledge of the hydric state of concrete is of utmost importance regarding the mechanical behavior and durability potential of concrete structures. From a microstructure perspective, the properties of moisture transfer is a manifestation of the internal pore structures. Therefore, it is also important to acquire the knowledge of the pore networks and the pore size distribution over a large range of the material.

In this thesis work, we investigate the moisturetransferring mechanisms in concrete with a combination approach of experiment and simulation. From the perspective of the drying model and the multi-scale structure of the concrete, we performed the experiments of drying, imbibition, and dryingimbibition cycles under controlled ambient condition for different geometries of concrete. The experimental work lasts over 200 days, obtaining the global mass variation and local inner humidity data. The moisture-transferring model contains two major mechanisms: liquid water permeation and water vapor diffusion. Based on the present model and the experimental results obtained, the simulation results of mass loss and relative humidity are calculated in CAST3M. In addition, an identification produce of parameters in the model is performed in an optimization program embedded in Matlab. A numerical-experimentidentification coupling method is thus proposed to simulate drying phenomenon, and the results provide a practical approach in following the moisture transfer process of concrete.

Following the parameters optimization, the hypothesis and assumptions in moisturetransferring model are discussed as well. The analysis includes the assumptions that are proposed in the model; a simplified analytic solution with the hypothesis of linear coefficient; and the moisture transferring pattern in the model, explaining if the two phases (liquid and vapor) of water interact in a parallel, series or combination style, how it influences the humidity profile and mass evolution.

The last part of investigation of the concrete is a multiple approaches to study the inner structure of concrete material, including mercury intrusion porosimetry method (MIP), computational X-Ray tomography, and focused ion beam-scanning electron microscope (FIB-SEM). By adopting these three techniques, we obtain the pore size distribution that covers a large range from tens of nanometers to few millimeters. Furthermore, the 3D visualization of the inner structures of the concrete material is reconstructed as well.

Acknowledgement

Life contains a series of experiences and journeys. The Ph.D. journey in France is so special and treasure for me. This is because not only the knowledge and expertise I obtained here, but also the unique and marvelous experiences I gained in my life. It is in many aspects different from my original culture so that I had both my ability improved and my vision expanded due the combination factors of the environment, the culture, the research work, as well as the exchanging and interactions with my supervisors, colleagues and friends.

Paris is a beautiful and open city with free and inclusive atmosphere, for which I appreciate a lot. I am lucky and grateful that I have spent four years in this city since 2016. I treasure so much the memory of this unforgettable journey and I want to express my sincere appreciations to those who ever helped and shared with me in this journey:

First of all, I would like to express my sincere appreciation to my supervisor Prof. Rachid Bennacer. My research work is greatly attributable to his constructive advice and valuable guidance, which reveals quite productive for the validation of my research. He introduced to me this wonderful university ENS-Paris-Saclay when I was preparing my master's degree in China and guided me to the lab of LMT with attentive care and help. It leads me to a completely different and brand new journey from my previous study, and I would appreciate in my life for all his effort and help to me.

I also gratefully acknowledge my co-supervisor Prof. Farid Benboudjema. During my research work, he provides me great support. Thanks to his patient and expertise guidance, which allows me to go further in both theory and programming aspects. He also helped to manage the administration process with external labs. Therefore I was able to go through my experimental and computational work smoothly. I would like to express many sincere thanks to all the jury members during my Ph.D. defense. Thanks to their professional questions and constructive suggestions, I got pleasant and fruitful discussion during the defense. Especially thanks to my reviewers: Sabine Caré and Abdelkarim Aït-Mokhtar, for their patient revisions and professional suggestions in improving the quality of my thesis.

As everything is difficult at the beginning, it was the same case for me. Thanks to Jérôme Carette, with whom I had done some cooperate work when he was post-Doc. I appreciate a lot for his kind help in the beginning of my research work. Special thanks also to Prof. Georges Nahas, for his assistance of allowing me to follow the CAST3M courses in the first semester.

I received also a lot of help from colleagues and technicians who helped me to prepare or perform my experiment work successfully. They are Kamilia Abahri, Aveline Darquennes, Rémi Legroux, Benjamin Smaniotto, Marc Bonnet from *LMT*, and Thomas Reiss, Elsa Vennat from the lab of *MSSMat*.

Furthermore, I would like to express my special thanks to Prof. Bin LIU, from Key Lab of Refrigeration Technology in Tianjin. He was my supervisor during my master study and encouraged in my research journey. Thanks to his support and recommendations, I won the selection and became the first graduate in university history to peruse PhD overseas with national scholarship.

In addition, I would like to acknowledge the CSC (China Scholoarship Councile), which support me financially during my four years study. Meanwhile, thanks to the European project *ThermSMART*, which allows me to carry on my research and exchange in conferences with other fellow researchers.

I can't agree more with the saying that friends is one of our best fortunes in life. I have my sincere thanks to the dear Chinese and French friends who have shared some journeys with me. They are Qiande Feng, Fei Mao, He Huang, Zuozei Zhu, Xin Wei, Wencan He, Jianfei Song, Younès and Xiaocui Boutinane, *etc.* The journal was more colorful because of these good friends. I wish them health and a prospective future in their respective fields.

In the end, particularly for my family, my gratitude is beyond words. I got unconditionally love and constantly support from my parents, my brother Jun MA, my friend Dejun Huang, Eric and Jenny Brooks and all my other family members. They encourage me with the greatest understanding and tolerance. They are the endless resource of my motivation and the strongest backup for my entire journey of life.

Contents

Li	st of	figure	S	vii
Li	st of	tables	5	xiii
Ν	omer	nclatur	e	xvii
1	Sub	ject b	ackground and thesis outline	1
	1.1	Envire	onment background concerning concrete applications	3
	1.2	Chara	cteristics of unsaturated porous media	4
		1.2.1	Basic definition of porous media	4
		1.2.2	Properties of humid air	6
		1.2.3	Physisorption isotherms of porous media	7
	1.3	Deteri	oration and transfer properties of concrete	8
		1.3.1	Deterioration of concrete	8
		1.3.2	Transport phenomenon in concrete	10
		1.3.3	WVSIs of concrete	12
	1.4	Outlin	ne of the thesis	13
2	Exp	oerime	ntal study of moisture transfer on drying, imbibition and	I
	dry	ing-im	bibition cycles	15
	2.1	Prepa	ration and curing of specimen	19
	2.2	Clima	te chamber and humidity sensors	21
		2.2.1	Climate chamber	21
		2.2.2	Temperature and humidity sensors	22
	2.3	Specir	nen grouping	23
	2.4	Result	ts and discussion	26
		2.4.1	Results in drying group	26

		2.4.2	Results in imbibition group	•	28
		2.4.3	Results in DI cycles group	•	30
		2.4.4	Results of internal humidity	•	33
	2.5	Conclu	usions	·	35
3	Sim	ulatio	n of moisture transfer and identification of parameters		39
	3.1	Assun	nptions and establishment of moisture transfer model \ldots .	•	41
		3.1.1	Hypothesis in the model and in simulations	•	41
		3.1.2	The derivation of moisture transfer model	•	41
	3.2	Nume	rical simulation with CAST3M	•	50
	3.3	Optim	nization of experimental method based on parameters analysis	•	52
		3.3.1	Positions of humidity sensors	•	54
		3.3.2	Levenberg-Marquart's minimization	•	54
	3.4	Result	s and discussion	•	57
		3.4.1	Results for prismatic lateral drying	•	57
		3.4.2	Results for cylindrical radius drying	•	63
	3.5	Conclu	usions	•	68
4	Hy	pothesi	is discussion on the moisture transfer model		71
	4.1	Simpli	ified analytical solution for drying	•	75
		4.1.1	Analogy between moisture and heat transfer problem	•	75
		4.1.2	Results of dimensionless analytical solution	•	80
		4.1.3	Validation of dimensionless transformation	•	82
		4.1.4	Comparison of analytical and nonlinear simulation results	•	84
	4.2	Simpli	ified analytical solution for drying-imbibition	•	87
	4.3	Model	assumption of two phases interactions	•	92
		4.3.1	Parallel-Series model assumptions	•	93
		4.3.2	The case of permeation dominating	•	95
		4.3.3	The case of two terms in the same level	•	99
	4.4	Conclu	usions	•	103
5	Mu	lti-scal	le study and 3D reconstruction of porous structures		105
	5.1	Mercu	ry Intrusion Porosimetry		111

	5.1.1	Introduction and principal of MIP	111
	5.1.2	Specimen preparation for MIP	112
	5.1.3	Penetrometer and devices	113
	5.1.4	Results and discussion for MIP	115
5.2	X-ray	Tomography test	118
	5.2.1	Introduction of X-ray tomography	118
	5.2.2	Samples preparation for tomography test	119
	5.2.3	Post-processing and 3D reconstruction of tomography results	120
5.3	FIB-S	EM test	125
	5.3.1	Introduction of FIB-SEM	125
	5.3.2	Equipment and sample preparation of FIB-SEM	126
	5.3.3	Results and 3D reconstruction of FIB-SEM results	128
5.4	Conclu	usions	129
Conclu	sions a	& Perspectives	133
Refere	nces		138
Appen	dix		138

List of Figures

1.1	Global cement and fossil energy production to 2016 [Andrew, 2018]	3
1.2	Cement production and cement-related CO_2 productions [Olivier and Pe-	
	ters, 2019]	4
1.3	Volume constitute of unsaturated porous media	5
1.4	Schematic diagram of representative elementary volume (REV)	6
1.5	Types of physisorption isotherms [IUPAC, 1985]	8
1.6	Types of hysteresis loops [IUPAC, 1985]	9
1.7	Hammurabi's code concerning responsibility toward durability of struc-	
	tures (dated to about 1754 BC)	9
1.8	Schematic of Darcy's experiment on water flow through sand [Darcy, 1856]	10
1.9	Water vapour desorption and adsorption isotherms measured at 23 $^{\circ}\mathrm{C}$ on	
	concretes and hcps, after sealed curing [Baroghel-Bouny, 2007a] \ldots .	12
2.1	All the test samples covered by aluminum foil	19
2.2	Climate chamber for samples in drying group	21
2.3	The storage bin - setup imbibition group	22
2.4	Temperature and humidity sensor (Ahlborn FHA 646)	22
2.5	schematic diagram of the sensor installed inside samples	23
2.6	Specimen dimensions and geometries in experiment	24
2.7	Relative mass loss in drying group for the two geometry patterns	27
2.8	Relative mass variation in drying group and mathematics fitting functions	
	in semi-logarithmic coordinates [Ma et al., 2017]	27
2.9	Results of mass increment in imbibition group for the two geometries	29
2.10	Results of mass increment per unit area in imbibition group for the two	
	geometries	29

2.11	Relative mass variation in DI cycles group with drying temperature of	
	38 °C, relative humidity of 32 $\%$	31
2.12	Relative mass variation in DI cycles group with drying temperature of	
	25 °C, relative humidity of 45 $\%$	31
2.13	Comparison of mass variation in DI cycles within the same time scale $\ . \ .$	32
2.14	Normalized mass variation in D-I cycles within the same time scale $\ .$	33
2.15	Relative humidity profiles in prismatic drying at different positions	34
2.16	Comparison of relative humidity at $1.5 \ cm$ to the drying surface in lateral	
	and radius drying	35
3.1	An example of meshing and sensors in prismatic samples	51
3.2	Identification algorithm flow chart [Ma et al., 2020]	53
3.3	Schematic diagram of sensors positions for the drying samples of two	
	geometries	54
3.4	Minimisation algorithm	56
3.5	Experimental and optimized simulation results of ML with illustration of	
	time window method in prismatic lateral drying $\ldots \ldots \ldots \ldots \ldots$	58
3.6	Experimental and optimized simulation results of RH, with illustration	
	of time window method in prismatic lateral drying	58
3.7	Relative variation of parameters versus time duration based ML for pris-	
	matic lateral drying	59
3.8	Relative variation of parameters versus time duration based ML for pris-	
	matic lateral drying (semi-logarithm coordinate)	59
3.9	Relative variation of parameters versus time duration based on ML with	
	one RH at position A and for prismatic	60
3.10	Relative variation of parameters versus time duration based on ML with	
	two RH points at position A and B for prismatic $\ldots \ldots \ldots \ldots \ldots$	61
3.11	Effect of sensor numbers and positions on relative variation of parameters	
	for prismatic case	62
3.12	Experimental and optimized simulation results of ML for cylinder radius	
	drying	63

3.13	Experimental and optimized simulation results of RH for cylinder radius drying $\ldots \ldots \ldots$	64
3.14	Relative variation of parameters versus time duration based on ML results	64
3.15	Relative variation of parameters versus time duration based on ML results (semi-logarithm coordinate) \ldots	6
3.16	Relative variation of parameters versus time duration based on ML and	
	RH point at position A for cylinder case $\ldots \ldots \ldots \ldots \ldots \ldots \ldots$	60
3.17	Relative variation of parameters versus time duration based on ML and	
	$R\!H$ point at position A for cylinder case (semi-logarithm coordinate) $$.	6
3.18	Effect of sensor numbers and positions on relative variation of parameters	
	for cylinder case	6
4.1	Schematic diagram of heat conduction problem in prism	7
4.2	Schematic diagram of heat conduction problem in cylinder \ldots .	7
4.3	Analytical dimensionless RH profile vs . dimensionless time (z) and space	
	(r)	8
4.4	Dimensionless RH evolution at different distances to drying surface for	
	prism	8
4.5	Dimensionless RH evolution at different distances to drying surface for	
	cylinder	8
4.6	Comparison of the analytical dimensionless RH with simulation results	
	calculated with constant coefficient at different positions for prismatic	8
4.7	Comparison of analytical dimensionless RH with simulation results cal-	
	culated with constant coefficient at different positions for cylinder $\ . \ . \ .$	8
4.8	Equivalent diffusion term and estimated value for prismatic and cylinder	8
4.9	Equivalent of heat capacity and estimated value for prismatic and cylinder	8
4.10	Comparison of the analytical solution and non-linear simulation results	
	for RH for prismatic sample \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots	8
4.11	Comparison of the analytical solution and the non-linear simulation re-	
	sults of RH for cylindrical sample $\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots$	8
4.12	Humid air diagram marking the two conditions in DI test	8
4.13	Illustration between sinusoidal external condition and square condition $\ $.	8

4.14	Analytical solution for DI periodic boundary (humidity or temperature
	profile) vs. time and space
4.15	Analytical fitting of mass variation in DI cycling for 25°C, 45 $\%~RH$ $~$ 91
4.16	Analytical fitting of mass variation in DI cycling for 38°C, 32 $\%~RH$ $~$ 91
4.17	Schematic diagram of transfer resistance in parallel and series way $[Ma$
	et al., 2018b]
4.18	Two contributions in diffusion coefficient profile (parallel case, $n=1)$ 95
4.19	Equivalent diffusion coefficient profile with different interpolation values
	for the permeation dominating case [Ma et al., 2018a]
4.20	Simulation result of ML with different interpolation values $\ldots \ldots \ldots 96$
4.21	Simulation result of RH with different interpolation values $\ldots \ldots \ldots 97$
4.22	Uniformed mass loss results with different interpolation values 99
4.23	Uniformed relative humidity with different interpolation values 99
4.24	Two contributions in diffusion coefficient profile for the similar level case 100
4.25	Equivalent diffusion coefficient profile with different interpolation values
	for the similar level case
4.26	Simulation result of ML with different interpolation values $\ldots \ldots \ldots \ldots \ldots 101$
4.27	Simulation result of RH with different interpolation values $\ldots \ldots \ldots \ldots \ldots 102$
5.1	Particle size and specific surface area related to concrete materials, mod-
	ified from [Sanchez and Sobolev, 2010]
5.2	Pore networks extracted from the 3D images [Blunt et al., 2013] 107
5.3	Process of FIB-SEM imaging: (a) aimed surface in 2D SEM; (b) cropped
	cross section of cement paste [Song et al., 2019]
5.4	A summary map illustrating the multi-scale methods and the correspond-
	ing scales
5.5	Schematic of mercury in equilibrium entering an opening under increasing
	forces [Corporation, 1996]
5.6	The prepared samples in MIP test
5.7	Illustration of penetrometer and the sealed sample cup with sample inside 114
5.8	Micromeritics AutoPore IV, Mercury Porosimeter (MSSMat, Centrale-
	Supélec)

5.9	Intrusion and extrusion curves in mercury intrusion porosimetry test $~$ 115 $$
5.10	Normalized cumulative intrusion curve in MIP
5.11	Pore size distribution of the three samples
5.12	A zoom in area of Fig. 5.11
5.13	X-ray tomography equipment X 50 (LMT, ENS Paris-Saclay) $\ldots \ldots 119$
5.14	Working principle of X-ray tomography [Light et al., 1994]
5.15	The tested sample in X-ray tomography
5.16	The global view of tested sample in X-ray tomography 120
5.17	Post-processing steps to extract spherical shape pores in X-ray tomogra-
	phy results
5.18	Post-processing steps: detect, find edges, and skeletonize analysis along
	with generate 3D structure
5.19	Reconstructed 3D view of bubbles in X-ray tomography results
5.20	Histogram of bubbles volume distribution in three samples
5.21	3D bubbles distributed in the sample $(760 \ pixel)^3$
5.22	3D bubbles distributed in the sample $(250 \ pixel)^3$
5.23	Schematic principle of electron and iron beam of FIB-SEM
5.24	Equipment of FIB-SEM
5.25	Concrete samples in FIB-SEM test
5.26	Ion beam image with magnification of 1200
5.27	Explanation of the electron image with magnification of 1502 129
5.28	A series of FIB-SEM figures on the scale of 11.5 μm , with resolution of
	20 $nm/pixel$ (575 is the total slides number of the image series) 129
5.29	The 3D reconstruction FEB-SEM view for a $(11.5 \ \mu m)^3$ cube with spatial
	resolution of $(20 \ nm)^3/voxel$

List of Tables

2.1	Mixing design of concrete B11	•	19
2.2	Main properties of concrete B11	•	20
3.1	Optimized parameters value for prismatic with mass loss data \ldots .	•	60
4.1	Summary of parameters in analytical solution	•	86
5.1	A summary of the MIP results		116
5.2	A summary of the statistic parameters in post-processing	•	124
5.3	Statistic counting of bubble diameters in X-ray tomography results		124

Nomenclature

Latin letters

Letters in lower case

a	thermal diffusivity	$m^2 \cdot s^{-1}$
a_{mq}, b_{mq}	parameter in M. Quirk equation	-
a_{vg}, b_{vg}	parameter in van Genuchten equation	-
d	diameter	m
d_c	critical pore diameter from MIP	m
С	concentration	wt%
c_p	specific heat capacity	$J\cdot kg^{-1}\cdot K^{-1}$
f_c, f_t	compressive, tensile strength	Pa
h	relative humidity	-
h_c	convective heat transfer coefficient	$W\cdot m^{-2}\cdot K^{-1}$
k_{la}	apparent permeability of liquid water	m^2
k_{rl}	relative permeability	-
m_x	specific mass of fluid	kg/m^3
m_{hyd}	specific mass of hydration water	kg/m^3
m_{vap}	specific mass of vaporized water	kg/m^3
p_a	air pressure	Pa
p_l	water pressure	Pa
p_v	vapor pressure	Pa
p_c	capillary pressure	Pa
p_{vs}	saturation vapor pressure	Pa
p_{krl}	parameter in van Genuchten equation	-
\mathbf{v}_{l}	mean velocity of water	$m \cdot s^{-1}$
\mathbf{v}_x	absolute velocity	$m \cdot s^{-1}$

Letters in uppercase

A	area	m^2
Bi	Biot number	-
D_0	intrinsic diffusivity of water vapor	$m^2 \cdot s^{-1}$
D_{va}	apparent diffusivity of water vapor	$m^2 \cdot s^{-1}$
E	Young's modulus	Pa
Ι	monochromatic X-ray intensity	$J\cdot cm^{-2}s^{-1}$
\mathbf{J}_1	mass flux of liquid water	$kg\cdot m^{-2}\cdot s^{-1}$
$\mathbf{J_v}$	mass flux of water vapor	$kg\cdot m^{-2}\cdot s^{-1}$
${f J}_{f v}^0$	mass flux of water vapor in plain air	$kg\cdot m^{-2}\cdot s^{-1}$
${ m J}_{ m v}^{ m mol}$	molar flux of vapor	$mol\cdot m^{-2}\cdot s^{-1}$
J_0, J_1	Bessel functions	-
K_0	intrinsic permeability of liquid	m^2
L	length	m
M_w	molar mass of water	$18 \ g \cdot mol^{-1}$
Q	flow rate	$kg\cdot m^{-2}\cdot s^{-1}$
R	perfect gas constant	$8.314 \ J \cdot kg^{-1} \ \cdot K$
S_l	saturation degree	-
Т	ambient temperature	K

Greek letters

γ	surface tension	$N\cdot m^{-1}$
λ	thermal conductivity	$W\cdot m^{-1}K^{-1}$
λ_n	element of eigenvalues vector	-
μ_l	dynamic viscosity of water	$Pa \cdot s$
$ ho_v$	density of water in vapor	$kg\cdot m^{-3}$
$ ho_l$	density of liquid water	$kg\cdot m^{-3}$
au	dimensionless time	-
Φ	porosity of the porous material	-

Abbreviations

C- S - H	Calcium Silicate Hydrate
D-I	Drying - Imbibition group of specimen
FIB-SEM	Focused Ion Beam -Scanning Electron Microscope
ML	Mass Loss
MIP	Mercury Intrusion Porosimetry
PSD	Pore Size Distribution
RH	Relative Humidity
RC	Reinforced Concrete
WVSIs	Water Vapor Sorption Isotherms

Chapter Subject background and thesis outline

Humans activities are influencing more and more the earth's climate in recent decades. A considerable proportion anthropogenic emissions of CO_2 to the atmosphere is from the cement production and related concrete industry. Therefore, the durability of concrete during its lifetime is of vital importance to the environment issue in a long term.

Studied show that the durability of concrete is closely related to the inner humid state of the material. Consequently, in our study we will perform a coupled experimentsimulation approach to study the moisture evolution of concrete.

In order to understand well this mechanism, we need the background knowledge of main properties of the concrete, and the moisture transport properties in cement-based materials. Being considered as a typical kind of porous material, concrete is also characterized by typical structure properties of porous media. Therefore, the background introduction of porous media will be presented as well.

As a summary, there are four sections in this chapter. In the first section, environment problem concerning concrete applications is proposed. In the second section, the characteristics of unsaturated porous media are introduced. In the third section, one of the significant challenge in its durability - structure deterioration or pathology is reviewed, and transfer properties of concrete are also presented. An outline of the thesis is described in the last part of this chapter.

1.1 Environment background concerning concrete applications

Humans are increasingly influencing the earth's climate by various production and life activities. Anthropogenic emissions of CO_2 to the atmosphere come from mainly three sources: the first is oxidation of fossil fuels, the second is deforestation and other land-use changes, and the third is carbonate decomposition. In recent decades, the global production of cement has become the third-largest source of CO_2 anthropogenic emissions, following the carbon dioxide emitted from fossil fuels and land-use change [Andrew, 2018].

Cement is a binding material that has been used since ancient times. The global cement and fossil energy production until the year of 2016 is presented in Fig. 1.1.



Figure 1.1: Global cement and fossil energy production to 2016 [Andrew, 2018]

It indicates that the global cement production has increased more than thirty times since 1950 and almost four times since 1990. In addition, the growth is much more rapid than global fossil energy production in the last two decades. In addition, the cement production and cement-related CO_2 productions during 2010 to 2017 is showed in Fig. 1.2.

In comparison to other engineering materials, *e.g.* steel, plastics, or ceramics, the micro-structure of concrete is characterized by inconstant property. This is because the bulk cement paste and the interface between cement paste and aggregate change over time [Kumar Mehta, 2006].

Historically, the word concrete comes from the Latin term *concretus*, and it means to grow. The strength of concrete relies on the quantity of the cement hydration products, and they continue to form for several years after fabrication, leading to a gradual



Figure 1.2: Cement production and cement-related CO_2 productions [Olivier and Peters, 2019]

enhancement of strength.

Scientists have explained some main reasons why concrete is the most widely used among engineering materials [Brunauer and Copeland, 1964]. Not only because the favorable property of being formed into a variety of shapes, but also that it is one of the cheapest and easiest available construction materials.

Such cheap material resists over time but several deterioration or disorders appears for different reasons. As it contains complex physical and chemical coupling, it is very difficult to predict all the evolution and pathology. One of the main reasons contributing to the difficulty is the multi-scale phenomenon occurring in such complex unsaturated porous media. We will present briefly some basic proprieties related to such unsaturated porous media.

1.2 Characteristics of unsaturated porous media

1.2.1 Basic definition of porous media

Porous media is a material characterized by the presence of a solid matrix, and a void phase that is presented by its porosity [Lu and Viljanen, 2011]. The skeletal material of porous media are often called the "matrix", and it is usually a solid phase. The pores are typically filled with fluid, either liquid or gas. Porous media are most often characterized by its porosity. Other properties of porous media like permeability, tensile strength, electrical conductivity, or tortuosity can be derived sometimes from respective properties of its constituents, porosity and pore structure. However such a derivation is usually complex. Some representative parameters of porous media will be introduced.

To have a global concept of unsaturated porous materials regarding with the volume proportion, it is proposed to understand the common model illustrating the relationship among pore volume, solid volume, volume occupied by water, and the volume occupied by dry air and vapor. The volume relationship is showed in Fig. 1.3.



Figure 1.3: Volume constitute of unsaturated porous media

It is clearly presented that the total volume V_t consists of solid volume V_s and pore volume V_p , and the pore volume is occupied by two kinds of constitutes: volume taken by liquid water (or ionic solution) V_l , and the volume taken by phase of gas, which consists of dry air and water vapor.

Based on this volume proportion, it is obvious to express the saturation degree $S_l = \frac{V_l}{V_p}$, the water content $w = \frac{m_w}{m_s}$, and also the total porosity $\Phi = \frac{V_p}{V_t}$.

In fact, porosity is an average property defined over the representative elementary volume (REV) [Bear, 1972]. As we plotted in Fig. 1.4, the porous media volume must be at least larger than the size of a single pore. When adding more pores, it will maintain a meaningful statistical average value. In the same time, it must be also smaller than the heterogeneity of the entire flow domain. Therefore, the representative elementary



Figure 1.4: Schematic diagram of representative elementary volume (REV)

volume provides an average porosity value for porous media over its domain.

The pore distribution allows to distinguish between several porous media with the same global porosity. The pore space is then considered in terms of individual pore size categories concept that enables quantification of its essential properties, which is consequence of such pore distribution and connectivity.

Some other basic definitions including tortuosity and specific surface area. Tortuosity is a property of a curve being tortuous. The quantification of such property is useful to describe diffusion and fluid flow in porous media. The mathematical expression to estimate tortuosity is the ratio length of the arc-chord to the distance separating the border of the arc-chord.

Specific surface area is a property of solids defined as the total external surface area of a material per unit of mass. Such property has a particular importance for adsorption or reactions on surfaces.

1.2.2 Properties of humid air

Porous media are considered dry if it contains no water molecular in porous structure. If exposed to humid air, the mixing of dry air and water vapor appears in varying proportions. Therefore the hygroscopic materials tend to vary their initial water state. Humid air is defined by its temperature and the body of water it contains. The moisture content is called absolute humidity, which remains constant. Moisture in air is mainly present in form of vapor and the maximum amount of vapor in air depends on the temperature strongly.

Relative humidity: If air is not fully saturated with moisture, the absolute humidity of air is lower than that at saturation level. Therefore, the relative humidity quantity hcan be defined as the ratio between the partial pressure of water vapor p_v (Pa) and the saturation vapor pressure p_{sat} (Pa) at the same temperature:

$$h = \frac{p_v}{p_{sat}} \tag{1.1}$$

This parameter is commonly named as relative humidity (RH). It expresses the equilibrium pressure between liquid and water vapor. It is an increasing function of temperature. A valid empirical expression is listed in Eq. 1.2, for $0 < T < 80^{\circ}$ C with a precision of $\pm 0.15\%$.

$$p_{sat}(T) = e^{23.5771 - \frac{4042.9}{T - 37.58}}$$
(1.2)

Where p_{sat} (Pa) is the saturated vapor pressure and T (K) is the absolute temperature.

From the viewpoint of thermodynamic, the total pressure is the sum of the partial pressure of each constituent of the mixture.

$$p = p_v + p_a \tag{1.3}$$

Considering humid air as the mixture of dry air and water vapor and assuming that these two gases follow the behavior of a perfect gas, the total pressure of humid air is the sum of the partial pressure water vapor p_v and the partial pressure of dry air p_a .

1.2.3 Physisorption isotherms of porous media

Physical properties of porous media are linked with their porous structure. The characterization of the porous structure is a prior step to predict physical behaviors of materials like hygrothermal and mechanical aspect. Various method have been developed to characterize porous structure [IUPAC, 1994], among them, intrusive methods and adsorption methods are the most widely used.

The quantity of gas adsorbed by physisorption depends on the surface area and the porous structure of the material. The IUPAC gives a classification of physisorption isotherms in six types, as showed in Fig. 1.5 [IUPAC, 1985]. Further more, a hysteresis may appear between adsorption and desorption branches. This hysteresis is often explained qualitatively by capillary condensation, existence of ink-bottle shaped pores, and more generally, interconnected pores spaces [Naono and Hakuman, 1993]. Like for physisorption isotherms, the IUPAC classifies hysteresis loops in four types (Fig. 1.6) and relates them with pore structures [IUPAC, 1985].



Figure 1.5: Types of physisorption isotherms [IUPAC, 1985]

1.3 Deterioration and transfer properties of concrete

1.3.1 Deterioration of concrete

Despite the outstanding properties of concrete, there are also some problems appearing in the lifetime of the concrete structures. As it is recorded almost four thousand years ago, the king of Babylon, Hammurabi, had formulated rules concerning the responsibility of builders, as presented in Fig. 1.7:



Figure 1.6: Types of hysteresis loops [IUPAC, 1985]



Figure 1.7: Hammurabi's code concerning responsibility toward durability of structures (dated to about 1754 BC)

"If a building falls down causing the death of the owner or his son, whichever may be the case, the builder or his son will be put to death. If the slave of the home owner dies, he shall be given a slave of the same value. If other possessions are destroyed, these shall be restored, and the damaged parts of the home shall be reconstructed at builder's cost."

Since engineers have to take the target service life into account, the durability of reinforced concrete is a main concern. It is of vital importance in some functional buildings, and there are various aspects that can deduce the deterioration of concrete structures. The intrusion of various type of ions, liquids and gases from the environment is the factors that cause the deterioration of concrete in an direct or indirect way. Studies show that the intrusion of carbon dioxide and chlorides would depassivate the steel in
concrete. And steel may start corroding in the presence of oxygen and water [Basheer et al., 2001].

However, in any situation, water is the ultimate carrier, either inside the concrete porosity or transport from external environment. Therefore, the research work on the moisture state of concrete and how it evolves over time is of vital importance.

1.3.2 Transport phenomenon in concrete

The movement of liquid gas, and ions inside concrete is important for the reason that they have physical or chemical interactions with concrete constituents. Thus it could change the composition of concrete, resulting in the deterioration of structures.

If we classify the transport by the driving forces and the nature of the matter, we can have the diffusion of water vapor, the permeation of liquid water and also the absorption that happened on the interface [Diment and Watson, 1985, Basheer et al., 2001]. In the present work, we will mainly focus on the permeation and diffusion phenomena.

Permeation expressed in Darcy's law

Darcy investigated the water flow through sand filters in order to purify water [Darcy, 1856]. His experimental apparatus is shown in Figure 1.8 by empirical observation.





through a porous material. The law can be expressed by Eq. 1.4.

$$v = \frac{Q}{A} = -\frac{k}{\mu} \frac{dP}{dL} \tag{1.4}$$

In which,

- v is the apparent velocity of flow, $(m \cdot s^{-1})$
- Q is the flow rate, $(kg \cdot m^{-2} \cdot s^{-1})$
- A is the cross-sectional area of flow, (m^2)
- k is a constant value, which referred to as the intrinsic permeability of the porous, (m^2)
- μ is the viscosity of the fluid, $(Pa \cdot s)$
- dP is the pressure loss over the flow path dL.

The intrinsic permeability k is characterized by the dimension of area, and the value only relies on the properties of the porous media. It means that it is independent of type and properties of the fluid.

This law is a generalized relationship of flow in porous media. It suggests that the volumetric flow rate is a function of the height, flow area, fluid pressure and a constant coefficient. Darcy's law can be stated in several forms depending on the flow conditions.

Permeability is thus defined as the property of a fluid media which characterizes the tendency to pass through it under the driving potential of pressure gradient [Katz and Thompson, 1986].

Diffusion of vapor expressed by Fick's law

If matter is transported from one part to another part of the domain because of the presence of concentration gradient, we call it diffusion process [Liu et al., 2011, Basheer et al., 2001]. The small random movement of the molecular causes the movement of the matter at the macroscopic scale.

The rate of mass transfer (mass flux J through unit area of a section is given by Fick's first law, which is proportional to the diffusion coefficient D and the concentration gradient $\frac{\delta c}{\delta x}$, as shown in Eq. 1.5 [Crank, 1975].

$$J = -D \,\frac{\delta c}{\delta x} \tag{1.5}$$

1.3.3 WVSIs of concrete

WVSIs means water vapor desorption and adsorption isotherms. It is the plotting of equilibrium mass water content of the hardened concrete versus relative humidity at a constant temperature [Baroghel-Bouny, 2007a]. A set of WVSIs curves obtained from the experiments on crushed specimens and concrete are plotted in Fig. 1.3.3.



Figure 1.9: Water vapour desorption and adsorption isotherms measured at 23 °C on concretes and hcps, after sealed curing [Baroghel-Bouny, 2007a]

As showed in Fig. 1.9, the main characteristic of WVSIs for concrete material is the hysteresis behavior, which means at the same relative humidity value, there is a difference in water content. The most studied reasons of the hysteresis in porous media include the variation in liquid-solid contact angle [Aligizaki, 2006], the ink-bottle effect [Espinosa and Franke, 2006, Brunauer, 1943, Bazant and Bažant, 2012], and the different spatial connectivity of pores in the drying and wetting processes.

Carlier [Carlier et al., 2012] evaluated different closed-forms of analytical WVSIs expressions used in soil science. They conclude that all models were able to represent the desorption isotherms for mortars and concretes correctly. Johannesson [Johannesson and Janz, 2009] and Derluyn [Derluyn et al., 2012] have adopted hysteresis models to study the hysteresis effects on moisture behavior of cementitious materials.

1.4 Outline of the thesis

From the general introduction above, we know that concrete as a kind of cementbased material, is considered as porous media. The hydrate state (or moisture content) in concrete plays an important role for the durability during its lifetime. Therefore it is necessary to simulate and predict the moisture state over time and space for this kind of material.

The precision of the prediction lies in the establishing theory of the model, the precision of the parameters in the model, and equally important, is the reliable and comprehensible database of experimental reference data. However, there are challenges and difficulties from different aspects in studying this problem. The most notable problems include: the non-consistence in existing literature of the controlling parameters in the model; the reliability and verification issues of the moisture transfer model, since several hypothesis were adopted to simplify and try to capture the main physics in moisture transfer problems; and at last but equally important, is the insufficient of long-term experimental databases for a variety of concrete of different component due to the time-consuming features.

Another prominent difficulty is that, during the lifetime of concrete, some key parameters (permeability, porosity, *etc.*) are not constant, but change with time and the environment ambient, since the pore structure of concrete evolves over time. It is a very slow but continuous process.

In the present work, consequently we investigate the moisture transfer phenomena of concrete in three parts: including experiment, simulation, and inner structure study.

The experimental work provides a reliable and comprehensive database for the specific concrete material. Numerical simulation is based on a moisture transfer model consisting two mechanisms(permeation and diffusion). Coupling with the experimental results, a optimization program is developed to identify the related parameters in the model. In addition, the coupling approach allows also to discover the optimization of experimental methodology based on a window duration analysis.

Due to the fact that the properties of material are strongly related to its pore network structures, we performed at last the multi-scale approaches to have an idea of the inner structures of concrete. The results cover a large scale of pore size and 3D views are obtained based on these method. It gives promising results and it is expectable to discover more the interlink between the micro structures with the macro-scale material properties.

Chapter **2**

Experimental study of moisture transfer on drying, imbibition and drying-imbibition cycles

As previously mentioned in Chapter One, the moisture transfer of concrete is a slow coupling process between the material and the environment. It is quite time-consuming to perform the experiments as in-site environment condition. Indeed, it is necessary to find a way to accelerate the transfer process in an experimental environment. Moreover, the experimental results are very important for understanding the moisture transfer mechanisms, as well as to quantify or modify the transfer model to have further and better predictions of moisture state of the concrete.

The studied material is named B11, which is hardened concrete and representative of an internal containment. It is used in the test for the fact that it is the same material as the concrete actually used in French internal nuclear power plant vessels [Hilaire, 2014]. The recorded parameters contain the global information (mass loss or mass increment throughout the sample) and the local information (relative humidity at specific positions of samples. One of the most widely used method for internal relative humidity is the insertion of humidity sensor in concrete [Granja et al., 2014].

By monitoring the moisture transfer parameters in the experiment, we can obtain accurate data for this kind of concrete. We can also build reliable database, both for analysis and simulation reference. Therefore, in this chapter, the experiments of moisture transfer in concrete are performed in the laboratory environment. The moisture transfer process include losing moisture from concrete, or gaining moisture from the ambient, and in some special applications gaining and losing water periodically (for example, bridge immersed in the sea). Considering the diverse environment conditions for concrete, we classified the samples and performed the test in three environment conditions: drying, imbibition, and drying-imbibition cycles.

One of the most important roles of experimental results is to provide database for numerical calculations. As our main goal is to capture the fundamental physics in moisture transfer process and to find the optimization of parameters in the model, it is more direct and less time-consuming to define the problem in one direction. Correspondingly, we will control the experiment on drying, imbibition, and cycles tests as one dimensional water transfer.

To ensure that, we follow the previous methodology by covering aluminum foil to prevent mass exchange on the lateral surfaces [Carette et al., 2020, Ma et al., 2017]. During the tests all the samples are wrapped tightly by aluminum on all the surfaces except the one exposed to humidity.

Especially, in the drying group, we adopt two geometries, prism and cylinder. The drying direction of prismatic sample is along the length direction (x), while cylindrical samples are drying along the radius direction (r). This allows us to investigate the different drying patterns and shape effect in drying phenomenon. The detailed geometries and sizes of specimen for each group and the exposure surfaces will be illustrated in Section 2.3.

In this chapter, firstly the preparation and preservation of the concrete specimen, along with the basic properties of the material are introduced. After that, the experimental devices and equipment such as climate chamber and humidity sensors are presented. Followed by that, we present specimen grouping and the environment conditions for each group. The experimental results for each group are presented and analyzed at the end of this chapter. In spite of encountering some difficulties in tracking inner humidity in concrete, we obtained some interesting results in each group. As a short conclusion, the main results in each group are presented below.

The results of mass loss over time in drying group indicates that moisture transfer follows adapted diffusion phenomenon for both lateral and cylindrical drying but needs geometry adjustment. Despite the diversity of mass increment in wetting group for different surface geometries, the fitting curves revealed an exponential increasing for both geometries. The results in drying-imbibition cycles present that after few cycles the mass variation curve became repetitive, which could reveal the geometrical redistribution equilibrium of humidity inside the inner structure of concrete. This limited period shows more complex phenomena which could be the air coupling flow and the inner evaporation condensation.

2.1 Preparation and curing of specimen

This section introduces the concrete material that is used in our experiments. The preparation process and conservation conditions are presented, and the main properties of the concrete are listed as well.

The reconstituted concrete B11 has been the subject of several scientific works and its basic properties have been widely investigated in previous studies [Omar, 2004, Briffaut et al., 2011, Hilaire, 2014]. It makes it possible to validate the experimental work and to characterize the variability of this concrete.

The mixing design of concrete B11 is listed in Table 2.1.

Integrates	$ ho~(t/m^3)$	B11 (kg/m^3)
Cement (CEM II Airvault Calcia)	3.1	366
Sand $(0/4)$	2.572	740
$\mathbf{Aggregates} \ (4/12.5)$	2.57	303
$\mathbf{Aggregates} \ (10/20)$	2.57	752
Water	1	193
Superplasticizer (Plastiment HP)	1.185	1.174

Table 2.1: Mixing design of concrete B11

The geometries and numbers of samples in each group are presented in Fig. 2.1.



Figure 2.1: All the test samples covered by aluminum foil

Demouling of the specimen is done one day after casting the concrete. For those samples subjected to drying, they are all tightly wrapped by one layer of plastic plus one layer of aluminum foil, to prevent any water exchange with air. The drying test begin after two months of conservation; Samples for imbibition test are placed in the open air for three months before the tests start.

From the casting and preserving process of the concrete samples, it is indicated that the samples are prevented from drying or any moisture exchange until the tests start, which is two months after mixing. Because of the high water-cement ratio of the B11 concrete (see Tabble 2.2), it can be considered that the hydration reactions are practically completed and consequently the auto-desiccation phenomenon can be neglected [Carette et al., 2016, Briffaut et al., 2011].

The initial state of the material for drying group considered almost saturated, due to the high w/c ratio of the material, and due to the fact that there was no water exchange with the ambient until the test began.

Property	Unit	Value
w/c	—	0.573
ho	t/m^3	2.324
Slump	cm	8 - 11
Porosity	%	13.2 - 13.8
f_c (28 days)	MPa	46.5
$f_t(28 \text{ days})$	MPa	3.29
E(28 days)	GPa	31.34

Table 2.2: Main properties of concrete B11

All the specimen are classified into three groups: Drying group (\mathbf{D}) , Imbibition group (\mathbf{I}) , and Drying /Imbibition cycle group (\mathbf{DI}) , based on surrounding conditions (temperature and humidity) during the test. The detailed information are presented in the next Section 2.3.

The specimens are monitored regularly of mass loss (\mathbf{ML}) , and for the specimen from drying group, the internal relative humidity (\mathbf{RH}) at specific positions are measured as well.

2.2 Climate chamber and humidity sensors

2.2.1 Climate chamber

The storage equipment for drying group samples is humidity chamber (Memmert HPP260). The model sizes are 64 $cm \times 80 \ cm \times 50 \ cm(weight \times height \times depth)$. It keeps constant temperature and humidity at the required level automatically. The temperature ranges from 5 °C to 70 °C, with the precision of ± 1 °C; and relative humidity ranges from 10 % to 90 %, with the precision of ± 0.5 %. The humidity chamber and the presented samples are shown in Fig. 2.2.



Figure 2.2: Climate chamber for samples in drying group

The storage container for samples in the imbibition group is a developed storage bin. The size is $800 \times 600 \times 220 mm^3$, which is shown in Fig. 2.3.

A plastic honeycomb board is placed on the bottom of the bin, in order to both support the specimen and keep minimum contact between the concrete surface and the water on the bottom. In addition, a glass cover is placed on the top of the bin, with sealing strip on the border of the glass cover, to insure the good sealing condition.

Due to the fact that pure water is filled on the bottom of the storage bin, it is supposed to remain the equilibrium humidity of 100 %. But in this imbibition test, the main purpose is to support the samples and to keep the exposure surface of specimen in continuous touch with the water below the honeycomb board.

Another advantage of this storage bin is that it could keep the inside ambient at a constant relative humidity by applying saturated saline solutions. Due to the sealability of the bin, it is possible to be without natural or forced convection, considering no air



Figure 2.3: The storage bin - setup imbibition group

movement inside the bin. The relative humidity in the box corresponds to the type and concentration of salt solutions at a certain temperature. The relationship of salt solution and relative humidity refers to Appendix A.

2.2.2 Temperature and humidity sensors

The sensor used in these experiments is a capacitive humidity sensor, (type Ahlborn FHA 646R), as presented in Fig. 2.4. These probes measure relative humidity and temperature at the same time. The application range for temperature is from -30 °C to +100 °C, with a precision of ± 0.1 °C. While for relative humidity, the test range is from 5 % to 98 %, with a precision of ± 2 % (when $RH \leq 90$ %). A preliminary tests for the response of relative humidity sensors in air was performed before the experimental work, the process and results refer to Appendix B.



Figure 2.4: Temperature and humidity sensor (Ahlborn FHA 646)

The sensors are inserted in holes which were drilled on hardened concrete in advance. This specific type of probe is chosen because of the small dimension (with probe diameter of 5 mm), and the broad operating relative humidity /temperature range and high accuracy. To reduce the risk of damaging the sample and the prob, the diameter of the holes are fixed at 6 mm, by drilling progressively from 3 mm to 6 mm. The scale and layout of the fixed sensors are shown in Fig. 2.5.



Figure 2.5: schematic diagram of the sensor installed inside samples

2.3 Specimen grouping

The test concrete samples are classified into three groups, with different geometries (cylinder and prism) and subjected to drying, imbibition and drying-imbibition cycles, respectively. The water variation of samples in all three groups are recorded by regular measurement of mass. Those samples subjected to drying group are monitored also by continuously recording of internal relative humidity.

As shown in the schematic Fig. 2.6, all the specimens are clarified into three groups, they are Group **D**, indicated to drying group; Group **I**, which is imbibition group; and Group **DI**, representing the drying-imbibition cycle group. The dimensions are given in Fig. 2.6 as well.

We take into account different geometries in the same group in order to investigate the shape effect during moisture transfer processes. The red-colored surface represents the free surface that is exposed to the surrounding environment (either in humid air or in contact with water). Chapter 2. Experimental study of moisture transfer on drying, imbibition and drying-imbibition cycles



Figure 2.6: Specimen dimensions and geometries in experiment

All the other surfaces are tightly wrapped by aluminum in order to avoid any evaporation and to ensure the moisture transfer in the expected direction. The environment condition and transfer direction for each group samples are specified in the following items.

1. Group of drying (\mathbf{D}) :

The samples subjected to drying are kept in the climate chamber (see Fig. 2.2). The ambient conditions inside the chamber is fixed at the temperature of 38 °C, and relative humidity of 32 %. There are six specimen with two different geometries. The shape and size of each geometry are illustrated as below:

- Prism named D1, with the dimension of 7 cm×7 cm×28 cm. There are totally three samples, two of them are measured by mass loss and one measured by inner humidity. The drying surfaces which are exposed to ambient are the two lateral surfaces (7 cm × 7 cm) marked with red color in Fig. 2.6. Four humidity sensors are inserted in the sample for humidity measurement, at the position of 1.5 cm, 3.0 cm, 6.0 cm and 9.0 cm from the drying surface, respectively.
- Cylinder named D2, with the diameter of 11 cm and height of 7 cm. There are three pieces in this case. The drying surface is the circular surfaces (the vertical ring), as shown in Fig. 2.6. Two of the samples are followed by mass

loss, and one for inner humidity. For the humidity measurements, two sensors are placed vertically in the sample, corresponding to $1.5 \ cm$ and $5.5 \ cm$ to the drying surface.

2. Group of imbibition (I):

Samples in the group of imbibition are placed in the storage bin, as shown in Fig. 2.3. There are three samples in total, with two different geometries: two prisms and one cylinder. They are initially dried in the air-conditioned room $(25 \,^{\circ}\text{C}, 45 \,\%)$ for three months before the test begins. All the external surfaces are covered by aluminum foil except the bottom surface, which is in contact with water. It allows one-directional water absorbing. The concrete specimen are arranged on the plastic honeycomb board inside the storage bin, to allow the maximum interaction with water on the bottom interface. The temperature in the climate bin is considered the same as the room temperature, which is controlled at 25 °C. The geometry and size of the samples are listed below:

- Prism named I1, 7 cm × 7 cm × 11 cm. The surface in contact with water is square side 7 cm × 7 cm, as shown in Fig. 2.6.
- Cylinder named I2 in Fig. 2.6, with the radius of 10 cm and height of 10 cm.
 It is the bottom circle surface that in direct contact with water during the imbibition test.
- 3. Group of drying-imbibition cycles (**DI**):

The environment condition of samples in the drying-imbibition group is the combination of drying test and imbibition test. Samples are placed firstly in the climate chamber to dry for ten days, and followed by another ten days of imbibition in the storage bin. It takes twenty days for each cycle, and there are totally six drying-imbibition cycles performed.

Regarding the geometry of samples, they are cylinders with the same dimensions as those used in imbibition group (radius of 10 cm and height of 10 cm), as shown in Fig. 2.6. The drying or imbibition surface is one circle surface marked in red, and other surfaces (top and vertical) are covered by aluminum foil by the same way.

In order to compare the effect of driving potential, we performed the dryingimbibition cycles with two different drying conditions independently. The environment conditions are presented as follow:

- Drying in climate chamber, with environment condition of 38 °C, 32 % RH, which is the same as the drying group; and imbibition test is in the storage bin, which is the same condition as imbibition group.
- Drying in the storage bin, with the temperature of 25 °C, which is the same as room temperature and relative humidity of 45 %, which is stabilized by saturated potassium carbonate solution on the bottom of the storage bin, without contact of the samples; while imbibition process in the cycle is the same as imbibition group.

2.4 Results and discussion

2.4.1 Results in drying group

The relative mass loss results in drying group for the two geometry patterns are shown in Fig. 2.7. The drying test lasts at least 162 days (test for inner humidity lasts longer than 200 days). For each geometry, two samples are included to guarantee the repeatability. The two geometries represent two different drying patterns: the lateral drying in prismatic samples, and the radius drying in cylinder samples.

As indicated in Fig. 2.7, the mass relative variation for cylinder case is much higher than the prismatic case. This phenomenon is attributed to two main aspects. Firstly, the original mass are different for the two geometries: the prism shape $(7 \ cm \times 7 \ cm \times 28 \ cm)$ is approximately twice the weight of cylinder shape $(\phi \ 11 \ cm \times 7 \ cm)$, and the relative mass loss is the variation of mass divided by the original mass of each geometry. Secondly, the drying surface for prism is the two lateral faces, while for cylinder is the circumferential surface with the radius drying pattern from all the external surface. Both aspects contribute to the fact that the mass loss of cylinder is much faster than the prism.

It is indicated also that the mass loss in the beginning has a higher gradient, especially for the radius drying in cylindrical samples. In the first 40 days, it drops sharply more



Figure 2.7: Relative mass loss in drying group for the two geometry patterns

than 3 % of the original mass, which accounts for approximately 80 % of all the mass loss during the 162 days of test. The variation gradient of mass loss decreases gradually afterwards.



Figure 2.8: Relative mass variation in drying group and mathematics fitting functions in semi-logarithmic coordinates [Ma et al., 2017]

In order to have a quantitative analysis of the drying process, the relative mass loss

results for the two drying patterns are re-plotted in semi-logarithmic coordinates, as shown in Fig. 2.8. For the prism samples, it is one-dimensional lateral drying, while for the cylinder samples, it is radial evaporating over time.

From the results and further analysis plotting, we can see that for the prismatic lateral drying, the mass loss of concrete follows a function of square root of time. A square root fitting function is plotted and the validity is obvious during the whole test period of 162 days. This is a consistent conclusion with the previous study [Carette et al., 2020]. While for the radial drying of cylinder, the mass loss fits with square root of time only in the very beginning of the drying period, which is less than ten days. In a long term, the mass loss curve of cylindrical samples fit a straight line in the semi-logarithmic coordinates plotting, which follows a logarithmic function of time.

The main difference between cylinder drying and lateral drying is the curvature effect. In cylindrical condition, the evaporating surface is not constant due to the drying section changes over time, while in lateral drying condition, the drying surface keep constant. It means that at the beginning of the drying process, the mass flux of both geometry are equivalent, and this period lasts approximately two days in current case; afterwards the effect of curvature appears gradually, and it is more and more obvious with time.

It indicates that the curvature effect doesn't appear at the beginning of drying period. Therefore, the mass loss follows the square root of time in the first few days. This can be explained that the thin layer variation is very small on the external surface, where the radius is biggest and the variation in curvature effect is so week that it could be negligible. As a result, it fits with the prismatic case. That is to say the section could be considered unchangeable section during the beginning period. So the drying profile for cylindrical case at the first period also follows the curve to square root of time. But the curvature increases more and more with the dry area going further and further.

2.4.2 Results in imbibition group

There are in total three samples in the imbibition group, one shape of cylinder, and two prisms. The imbibition tests are considered as one dimensional for all the samples. The duration of imbibition test is 125 days. The results of mass increment for cylinder and the average value of the two prism specimens with error bars are presented in Fig. 2.9.



Figure 2.9: Results of mass increment in imbibition group for the two geometries

It is worth noticing that despite the two different geometries of samples, they are with the same wetting pattern, which is one-dimension from bottom to top. This is because that all the samples are immersed in water with one lateral surface, and all the other surfaces are tightly covered by aluminum foil. For cylinder samples, the exposed surface that is in contact with water is a circle shape, whereas for the prismatic samples is a square surface, as previously mentioned with the red-colored surfaces in Fig. 2.6.



Figure 2.10: Results of mass increment per unit area in imbibition group for the two geometries

Results of mass increment in imbibition group show diversity for specimens with different surface shapes. For the two samples with the same section surface in prism group, the standard derivation of water mass increases with time, and reaches 3.6 % at the end of the period of the test. As it is calculated from the absolute mass increment divided by the initial mass of the specimen, it is a relative water variation for unit mass. Considering the different shapes of the wetting surface, the surface area could be one of the factors contributing to the diversity. Therefore, the mass increment on unit section area is calculated and plotted in logarithm coordinates, as shown in Fig. 2.10.

In the logarithmic coordinates, it is revealed that for both geometries the water increment follow linear trend, which indicates an exponential increasing. The fitting curves show an index of 0.25 for both geometries. However, there is still a slope diversity in the fitting curve, which remains under discussion.

2.4.3 Results in DI cycles group

Two sets of data are obtained in the **DI** cycle tests, corresponding to the two different controlled environment conditions. In the first cycle set, the drying conditions are 38 °C, 45 % which is the same as the drying group. In comparison, the second cycle set has the drying environment of 25 °C, 45 % RH. However, imbibition condition is the same for the two cycles groups, which is one surface in contact with water in the room temperature of 25 °C in the storage bin.

The total duration of each set is 120 days with six cycles of drying-imbibition. The relative mass variation curves for the two sets of test are presented in Fig. 2.11 and Fig. 2.12, respectively.

It is obviously shown in the result that the first drying-imbibition cycle has a largest variation range in comparison with the following five cycles. It is almost the same pattern for both of the cycles groups. For the drying ambient of 38 °C, 32 % RH, the mass loss in the first dying reaches 1.17 %, while for the drying ambient of 25 °C, 45 % RH, the maximum mass loss at the end of first drying period is 0.82 %.

Another interesting phenomenon is that, in the first DI cycle, the duration of drying and imbibition is the same duration, but the water absorbed is unable to recover the same quantity of what it lost during the drying process. For both ambient conditions, the difference is the same, i.e. about 0.2 % of the original mass.



Figure 2.11: Relative mass variation in DI cycles group with drying temperature of 38 °C, relative humidity of 32 %



Figure 2.12: Relative mass variation in DI cycles group with drying temperature of 25 °C, relative humidity of 45 %

In Fig. 2.11 and Fig. 2.12, the mass variation during the six drying-imbibition cycles appears similar damping trend, especially in the first three cycles, and the last few cycles tend to be the same range.

To have an overview of all these six cycles, it is indicated that the gradient is higher in the beginning of drying or imbibition process. The rate to lose or to gain water tends to slow down at the end of the ten days. and they display similar tendency for all the six cycles. As shown in Fig. 2.11 and Fig. 2.12, it tends to be in smaller and smaller range of mass change for the first three cycles, afterwards tend to be constant both in ranges and in profiles at the end of the cycles (the last three cycles). That is to say, they are repetitive and reach relatively the equilibrium condition under this environment condition.

In order to compare all the cycles in the same time scale, we re-plot the relative mass variation in each drying imbibition cycle within one period of approximately 20 days, as shown in Fig. 2.13.



Figure 2.13: Comparison of mass variation in DI cycles within the same time scale

Because of the phenomenon that each DI cycle has its own mass variation range, it it difficult to capture the common physics. To confine them in the same range, we deduced the normalized mass variation value (the mass variation in each cycle divided by its own maximum range) and the result is shown in Fig. 2.14. We can see that the drying and imbibition are repeatable in tendency, with more clear behavior on imbibition branch.

It is suggested that the absorbed moisture mass is maximum in the first cycle, so does the evaporated moisture mass. For the following three cycles, the peak value of the water loss decrease continuously, but the ends of the imbibition are relatively the same. Afterwards, the three following cycles have almost the same profile of mass variation, which implies that the porous structure in the material is not changing anymore. It



Figure 2.14: Normalized mass variation in D-I cycles within the same time scale

indicates that the absorption - desorption mechanism is relative stable, and the relative equilibrium state is reached after four cycles.

Results from the normalized mass variation curve presented consistent trend for all the six cycles. They follow similar profiles for both drying and imbibition periods. The fitting curve for drying period presents a fitting curve of $e^{t^{0.37}}/10$, while for the imbibition period it is $1 - [(t - 10)^{0.5}]/3.5$.

During the drying process of first three cycles, as the desorption happens by means of evaporation, so liquid water content decrease, the permeability of liquid water decrease [Baroghel-Bouny, 2007b]. This phenomenon along with the smaller difference in humidity between the surface and ambient both result in a lower value of the evaporation rate in the following days of drying. Furthermore, small cracks could appear during drying process and the change in structure could allow more water molecular to cluster on the interface of the micro-scale cracks, leading to vary the ability of absorption or desorption of water.

2.4.4 Results of internal humidity

The monitor of relative humidity inside concrete is performed in the drying group, for both prism and cylinder geometries. The inner humidity profile for prismatic geometry at four test points is presented in Fig. 2.15.



Figure 2.15: Relative humidity profiles in prismatic drying at different positions

The dashed line on top presenting relative humidity of 100 % is considered as the initial inner humidity, and the red dashed line on bottom presenting relative humidity of 32 % is the ambient relative humidity. As it is indicated in Fig. 2.15, the inner relative humidity at different positions will decrease over time. Meanwhile, at any time point, the gradient of humidity always exists. This is the potential force to keep moisture moving over time.

This is logical because at the early time the sample is saturated over the domain. As we imposed 32 % relative humidity on the external surface, we observe a common diffusion front (see the blue arrow in Fig. 2.15). This front evolves toward the bulk over time. After 60 days we can see that the skin concerned by the drying process covers already 9 cm.

We notice also that some data points are lost at the position of 9.0 cm and 6.0 cm to drying surface. These two positions are in the relative center position of the specimen, so the relative humidity could keep a relative higher level (close to 100 %). However it is outside the sensor's measuring range, and the high content of moisture around makes it invalid.

To compare the inner humidity at the same position for the two different drying patterns (prismatic lateral drying and cylindrical radius drying), the humidity profile at $1.5 \ cm$ to the drying surface is plotted for both geometries, as shown in Fig. 2.16.



Figure 2.16: Comparison of relative humidity at $1.5 \ cm$ to the drying surface in lateral and radius drying

We noticed that the drying rate for cylindrical sample is higher than the prismatic sample. The radius drying reaches the ambient humidity at about 150 days, but the lateral drying still remains higher than 40 % at the end of the test time. This relative humidity profile is coherent with the mass loss evolution as we discussed previously (see Fig. 2.7. Because the mass loss is an integral value over the whole samples, it is related to the variation of the local relative humidity change.

The fast decreasing of inner humidity for cylinder is a consequence of the curvature effect and also for the limited reservoir. When the front became close to the bulk center, the water contents decrease and it remains less and less reservoir to support the diffusion process as in the semi infinity domain.

All the experimental results of mass variation and relative humidity will be regarded as the database for parameters optimization in simulation process. More details results for relative humidity will be discussed in Chapter Three.

2.5 Conclusions

In this chapter, the experimental work of moisture transfer in concrete specimen is conducted. There are in total three groups of tests to investigate moisture transfer mechanisms. They are group of drying, group of imbibition and group of drying-imbibition cycles. In drying group, the moisture variation is monitored by two approaches: mass loss and inner humidity. The other two groups are followed only by the variation of mass. The geometry effect is also taken into consideration. The main results are concluded as below.

• Drying group:

In the drying group, the automatic humidity chamber is adopted and the environment conditions inside the chamber is constant at the temperature of 38 °C, and relative humidity of 32 %. The test duration lasts at least 162 days. The two geometries of concrete samples characterize two different drying patterns: the lateral drying in prismatic shape, and the radius drying in cylindrical shape.

Results shows that the relative mass loss for cylinder case is much higher than the prism case, and the mass loss in the beginning has a higher gradient, especially for the radius drying in cylindrical samples. To be specific, for the prism lateral drying, the mass loss of concrete follows the function of square root of time, while for the radial drying of cylinder, the mass loss fits with square root of time only in the very begging of the drying period, which is less than ten days. It follows a logarithmic function versus time afterward.

The main difference between radius drying and lateral drying is considered as the curvature effect and the limited reservoir as we get out of the semi infinity approach. The results of mass loss over time indicate that moisture transfer in drying group follows adapted diffusion phenomenon for both lateral and radius drying, meanwhile geometry factors account for the differences between the two different drying patterns.

• Imbibition group:

Samples in the group of imbibition are placed in an enclosed storage bin with honeycomb board on the bottom, which allows the contact of concrete surface with water. Three samples are considered to study one-dimensional water absorbing dynamics. The ambient temperature is 25°C, and the duration of the water absorption test is 125 days.

Despite the two different geometries of samples, both are one-dimensional water transport pattern from bottom to top. In these two tests, we have both longitudinal moisture transfer and no curvature effect. This test look the goal of two mould and lateral surface in order to quantify the mass flux. Results of mass increment show diversity for specimen with different surface geometry and also the same shape in prism group. The fitting curves revealed that for both geometries the water increment follow linear trend in logarithm coordinates, which implies a polynomial increment. There is more to be explained about the slope diversity for different samples.

• DI cycles group:

The drying-imbibition cycles group is performed with two sets of environment conditions for drying period: one is 38 °C, 32 % RH, the other is 25 °C, 45 % RH. But he imbibition conditions are the same, with ambient temperature at 25 °C. Each cycle lasts 20 days consisting of 10 days of drying and another 10 days of imbibition. There are six cycles carried out for both environment conditions.

Mass variation curve shows that mass loss is faster at the beginning of each drying cycle and so does mass gained at the beginning of imbibition cycles. In addition, the first drying-imbibition cycle covers the largest variation range in comparison with the following five cycles. The water absorbed in the first cycle recovered less than what it lost in the drying for both environment conditions.

Furthermore, the mass variation in the six cycles exhibit similar a damping trend: for the first three cycles, the variation range is smaller and smaller, afterwards it tend to be constant at the end of the cycle. This interesting phenomenon reveals the tendency became repetitive after few cycles, which indicates the equilibrium condition could be reached after several cycles of drying-imbibition. The main challenges include to explain the reasons of such non-symmetrical behavior and to quantify the local properties, allowing the prediction or simulation if adequate and reliable model exists.

Chapter 3 Simulation of moisture transfer and identification of parameters

The previous Chapter 2 explained the experimental method to quantify the moisture transfer in concrete samples by following both the global mass variation and local humidity information. It also allows to quantify the imbibition and the drying-imbibition coupling.

These results provide a valuable database on mass loss and inner humidity. However the experiments in lab ambient is limited by the size and numbers of specimen. Furthermore, the time-consuming and high-cost characters require to predict the moisture evolution by more reliable substitute methods, *e.g.* computational approach, and also analytical solution to explain the tendency (this part will be discussed in Chapter 4).

Therefore in this chapter, we will begin with the simulation study. Firstly, the deducing drying model is presented. Some assumptions adopted in the model and in the numerical calculation are also presented. The numerical work is compared mainly with the results in drying group, for the reason that data obtained in drying group include both mass loss and relative humidity, and two different drying patterns are performed for comparison. However, the model is supposed to be valid for imbibition process as well.

Afterwards, the computational approach to calculate humidity and mass loss evolution (versus time and space) is illustrated, including the related parameters and imposed boundary conditions. Due to the fact that the related parameters in the model could significantly influence the computational results, and most of them are not consistent in existing literature. Therefore, we carried out an identification process based on the coupling of experiment and simulation results. At last, by adopting this identification approach, a numerical-experiment-identification coupling method is proposed to find out how the parameters change with the experimental test duration. Furthermore, the prediction of the optimal experimental methodology (test duration, sample geometry, number and positions of humidity sensor) will be analyzed based on this coupling approach and different test durations.

The results can be shortly summarized as: in order to follow and predict the humidity profile inside concrete, the test of only mass loss is not sufficient to get precise parameters to be applied in the drying model, at least one sensor information is necessary to predict the drying profile. If only one sensor is used in detecting the inner relative humidity evolution, the position, which is closer to the drying surface, is better than further ones. Nevertheless, in reality, it is also dependent on the fixing technique of the sensors.

The majority content of this chapter was published in the journal of *Construction* and *Building Materials* [Ma et al., 2020].

3.1 Assumptions and establishment of moisture transfer model

3.1.1 Hypothesis in the model and in simulations

The moisture transfer model in this study is based on several assumptions, in order to capture the dominate physics and simplify the problem reasonably. The following assumptions are made in this study:

- At any point of continuous and unsaturated porous media, the different phases: solid, liquid are in local thermodynamic equilibrium;
- The air inside the porosity is considered as inert and not contributing to the model. It means that the transport of vapor water by advection of gas is negligible, and gas pressure in the pores is assumed to be equal to atmosphere pressure (considering no displacement of gas);
- The solid media is non-deformable. The solid phase is considered as isotropic material, and the concrete is already hardened, meaning that there is no more chemical reaction (hydration process) between the concrete and moisture;
- Moisture transfer is considered in two forms: permeation of liquid and diffusion of vapor. Each of them takes the displacement on its own local domain and no interaction with one and the other; *i.e.* there is no condensation - evaporation on alternative liquid bridges;
- Convection and radiation heat transfer are negligible;
- The transfer of moisture under the effect of gravity is negligible.

3.1.2 The derivation of moisture transfer model

The transfer physics and the derivation process of the moisture transfer model is described in this section. As it is illustrated in Chapter 1, the moisture transfer process in porous media is a very complex phenomenon, due to the fact that it contains sorptiondesorption coupling, permeation of liquid water, diffusion of water vapor, as well as evaporation and condensation.

At the ambient temperature for cementitious materials, we consider that two mechanisms play predominant roles in the water transfer process, they are the permeation of liquid water and diffusion of water vapor. The gas pressure is considered as constant. Baroghel-Bouny's study [Baroghel-bouny,V., 1994] also verified this assumption that when the drying process is under the intermediate temperatures ($RH \approx 50 \%$, $T \approx 20^{\circ}C$), the predominate factors are permeability of liquid water and the diffusivity of water vapor.

As a matter of fact, three constituents are filled in the voids of the porous media, they are liquid water, water vapor and gas (dry air). From the point of view of mass conservation of liquid, vapor and air, the following Eq. 3.1 can be obtained:

$$\dot{m}_{l} + div (m_{l} \cdot \mathbf{v}_{l}) = -\dot{m}_{vap} - \dot{m}_{hyd}$$

$$\dot{m}_{v} + div (m_{v} \cdot \mathbf{v}_{v}) = \dot{m}_{vap}$$

$$\dot{m}_{a} + div (m_{a} \cdot \mathbf{v}_{a}) = 0$$
(3.1)

in which,

- $m_x(x = l, v, a)$ is the mass (per unit volume) of fluid (kg/m^3), and $m_x = \rho_x \Phi S_x$
- m_{hyd} is the mass (per unit volume) of liquid water that is consumed during the hydration reaction (kg/m^3)
- m_{vap} is the mass (per unit volume) of water vapor (kg/m^3)
- \mathbf{v}_x is the absolute velocity of the corresponding fluid ($m\cdot s^{-1}$)

Taking into consideration the assumptions mentioned above, the third equation in Eq. 3.1 can be eliminated, and $m_{hyd} = 0$ due to the fact that hydration process is considered finished. Therefore, Eq. 3.1 will be simplified the following Eq. 3.2.

$$\dot{m}_{l} + div \left(m_{l} \cdot \mathbf{v}_{l} \right) = -\dot{m}_{vap}$$

$$\dot{m}_{v} + div \left(m_{v} \cdot \mathbf{v}_{v} \right) = \dot{m}_{vap}$$

$$(3.2)$$

Combining these two equations, we deduce Eq. 3.3:

$$\dot{m}_l + \dot{m}_v + div\left(m_l \cdot \mathbf{v}_l + m_v \cdot \mathbf{v}_v\right) = 0 \tag{3.3}$$

Equation 3.3 is the original format of the moisture transfer model. In order to uniform the mass flux of liquid and vapor, we unfold the mass flux terms based on physical meaning, so as to reduce the number of variables in this equation.

For the mass derivative of each phase:

It can be expressed by a function of saturation degree S_l , porosity Φ and corresponding densities ρ_l , ρ_v , which is given by Eq. 3.4:

$$m_l = \rho_l \cdot \Phi \cdot S_l$$

$$m_v = \rho_v \cdot \Phi \cdot (1 - S_l)$$
(3.4)

In which,

- Φ is porosity of the porous material, (%)
- S_l is saturation degree of liquid water in the unsaturated material, (%)
- $-\rho_x$ is the density of liquid or vapor water, ($kg \cdot m^{-3}$)

Therefore the derivative of quality versus time can be expressed as Eq. 3.5.

$$\dot{m}_l + \dot{m}_v = \rho_l \cdot \Phi \; \frac{\partial S_l}{\partial t} - \rho_v \cdot \Phi \frac{\partial S_l}{\partial t} = \rho_l \cdot \Phi \; \left(1 - \frac{\rho_v}{\rho_l}\right) \frac{dS_l}{dt} \tag{3.5}$$

For the flux of liquid water:

In a fully saturated isotropic porous media, if the gradient of hydro-static pressure is not zero, it will induce the flow of fluid inside the pore networks. In order to relate the mean velocity v_l^0 of the supposed laminar flow with the gradient of water pressure p_l , Darcy's law (Eq. 3.6) provide the formula by the intrinsic permeability K_0 , and the dynamic viscosity μ_l . For a single-phase flow, the intrinsic permeability is independent from the fluid that is filling up the porous network, which means that the measured permeability is identical whatever the fluid used to measure it.

$$\mathbf{v_l^0} = -\frac{K_0}{\mu_l} \ \nabla p_l \tag{3.6}$$

In which,

– $\mathbf{v_l^0}$ is the mean velocity of water in saturated porous media, ($m\cdot s^{-1}$)

- p_l is the water pressure, (Pa)
- K_0 is intrinsic permeability of liquid flowing in saturated porous media, (m^2)
- $-\mu_l$ is the dynamic viscosity of water, ($Pa \cdot s$)

However, the partially saturated porous network makes it complicate to model the transfer mechanisms, so the relations proposed above (Eq. 3.6) need to be adopted accordingly. The determining factor is supposed to be the saturation degree of the material: with a high saturation degree, the pore network is predominantly occupied with liquid water, and a wide path of liquid network allows water to communicate with the external environment. Conversely, if the saturation degree is low, diffusivity of vapor phase will be the main drying force. Therefore, the intrinsic permeability is modified by multiplying a coefficient, relative permeability k_{rl} , which is related to the saturation degree of the porous media.

Consequently, Eq. 3.6 in a partially saturated material can be expressed by Eq. 3.7:

$$\mathbf{v_l} = -k_{rl} \; \frac{K_0}{\mu_l} \; \nabla p_l \tag{3.7}$$

The new parameter k_{la} is defined as apparent permeability of liquid:

$$k_{la} = k_{rl} K_0 \tag{3.8}$$

Therefore the mass flux \mathbf{J}_1 of the liquid water is expressed by Eq.3.9. In order to simplify the format of this expression, the apparent permeability k_{la} is used to replace intrinsic permeability K_0 multiplied by relative permeability k_{rl} :

$$\mathbf{J}_{1} = m_{l} \mathbf{v}_{l} = -\rho_{l} \frac{k_{rl} \cdot K_{0}}{\mu_{l}} \nabla p_{l} = -\rho_{l} \frac{k_{la}}{\mu_{l}} \nabla p_{l}$$
(3.9)

In which,

- ${\bf J}_{\bf l}$ is the mass flux of liquid water, ($kg\cdot m^{-2}\cdot s^{-1}$)
- $\mathbf{v_l}$ is the mean velocity of water in unsaturated porous media, ($m \cdot s^{-1}$)
- k_{la} is the apparent permeability of liquid, (m^2)

For the flux of water vapor:

In humid air, water molecules exist in the form of water vapor. If the water molecules' molar concentration is not uniform throughout the zone filled with vapor, the molecules will move from the high density to the low-density position.

In the open air, the molar flux of water molecules in still air (J_v^{mol}) can be expressed by Fick's law, as Eq. 3.10 [Crank, 1975]. In addition, based on the assumption that the water vapor is perfect gas, the mass flow of vapor J_v^0 could be expressed as a function of the vapor pressure, Eq. 3.11.

$$\mathbf{J}_{\mathbf{v}}^{\mathbf{mol}} = - D_0 \ \nabla c \tag{3.10}$$

$$\mathbf{J_v^0} = - D_0 \; \frac{M_v}{R \; T} \; \nabla p_v \tag{3.11}$$

where,

- D_0 is the intrinsic diffusivity of water vapor, ($m^2 \cdot s^{-1}$)
- $\mathbf{J}_{\mathbf{v}}^{\mathbf{mol}}$ is the molar flux of vapor ($mol \cdot m^{-2} \cdot s^{-1}$)
- ${\bf J_v^0}$ is the mass flux of the water vapor in plain air, ($kg\cdot m^{-2}\cdot s^{-1}$)
- $-p_v$ is the vapor pressure, (Pa)
- M_v is the molar mass of the water, ($18\times 10^{-3}~kg\cdot mol^{-1}$)
- R the perfect gas constant, ($8.314~J\cdot kg^{-1}~\cdot K)$
- T the ambient temperature in Kelvin, (K)

Regarding to the unsaturated porous media, the vapor diffusivity is not simply equal to the vapor diffusivity in the air [Troeh et al., 1982]. The geometry factors of the porous network must be taken into consideration, including the tortuosity of the pore networks, the porosity of the materials, as well as the ratio of unconnected pores. Instead of intrinsic diffusivity D_0 , an apparent diffusivity is considered to modify the flux. The apparent diffusivity (or effective diffusivity) D_{va} is therefore related to the saturation degree, porosity and tortuosity of the porous structures. So far, the mass flux of water vapor will be deduced by the following formula 3.12:
$$\mathbf{J}_{\mathbf{v}} = m_l \ \mathbf{v}_l = - \ D_{va} \ \frac{M_v}{R \ T} \ \nabla p_v \tag{3.12}$$

in which,

- $\mathbf{J_v}$ is the mass flux of water vapor in unsaturated porous media, ($kg \cdot m^{-2} \cdot s^{-1}$)

- D_{va} is apparent diffusivity of water vapor, ($m^2 \cdot s^{-1}$)

Uniform of driving forces

The displacement of water for both phases is due to the pressure gradient over space, the pressure difference is therefore considered as the driving force of the moisture transfer process. However, the local pressure is not a parameter that can be directly measured, which increase the difficulties to compare with experimental results. In comparison, the relative humidity (RH) is used to describe the desiccation of concrete. It is a locally – defined parameter, which makes it possible to describe the energy state of the water in the pore structures. The relative humidity permits to definite the thermodynamic equilibrium between two phases of water - liquid and gaseous phase.

Accordingly, the modified Kelvin equation (Eq. 3.13) indicates that the relative humidity can be related to capillary pressure. Consequently, the evolution of humidity is reflected in the variation of capillary pressure.

$$p_c = -\rho_l \, \frac{R \, T}{M_w} \, \ln(h) \tag{3.13}$$

where,

- M_w is the molar mass of water, ($18 \times 10^{-3} \ kg \cdot mol^{-1}$)
- $-p_c$ is the capillary pressure, (Pa)
- h is the relative humidity, (0 < h < 1)
- $-\rho_l$ is the density of liquid water, (1000 kg $\cdot m^{-3}$)

Equation 3.13 indicates that the modified Kelvin equation relates the pressure difference between the liquid and the atmosphere to the relative humidity h. Therefore, the derivative of capillary pressure versus relative humidity is expressed by Eq. 3.16:

$$\nabla p_c = -\frac{1}{h} \cdot \rho_l \cdot \frac{R T}{M_w} \nabla(h)$$
(3.14)

In accordance with the definition of relative humidity 3.15, it is the ratio of vapor pressure over the saturated vapor pressure under the standard status:

$$h = \frac{p_v}{p_{vs}} \tag{3.15}$$

in which,

- p_v is the local vapor pressure, (Pa)
- p_{vs} is the saturation vapor pressure at atmosphere pressure of 2333 Pa and temperature of 25 °C, (Pa)

The Kelvin's law provides a function between capillary pressure and relative humidity. Combining the definition of relative humidity, we can also obtain the relationship between capillary pressure and vapor pressure.

From Eq. 3.15, we have the gradient p_v with respect to gradient of relative humidity h, which is Eq. 3.16

$$\nabla p_v = p_{vs} \cdot \nabla(h) \tag{3.16}$$

Concerning the relationship between capillary pressure and liquid pressure, we insert the definition of the capillary pressure in a capillary pore, which is the pressure difference between the external atmosphere pressure p_{atm} and the internal liquid pressure p_l at the liquid-air interface. This is given by the following equation 3.17:

$$p_c = p_{atm} - p_l \tag{3.17}$$

In this case, we consider the atmosphere pressure is constant. Consequently, the gradient of liquid water pressure is described by equation 3.18:

$$\nabla p_l = -\nabla p_c = \frac{\rho_l}{h} \frac{R T}{M_w} \nabla(h)$$
(3.18)

As a result, the pressure gradient for vapor and liquid can be expressed uniformly by the gradient relative humidity h.

Substituting Eq. 3.16 and Eq. 3.18 into Eq. 3.12, and Eq. 3.9, respectively, we obtain the final expression of the mass flux of liquid water and water vapor:

$$\mathbf{J}_{\mathbf{l}} = m_l \ \mathbf{v}_l = -\frac{k_{la}}{h} \ \frac{\rho_l^2}{\mu_l} \cdot \frac{R \ T}{M_w} \ \nabla(h) \tag{3.19}$$

$$\mathbf{J}_{\mathbf{v}} = m_v \ \mathbf{v}_v = - \ D_{va} \cdot p_{vs} \ \frac{M_v}{R \ T} \ \nabla(h)$$
(3.20)

Finally, by substituting equation 3.20, 3.19 and 3.4 into equation 3.3, we reach the format of the moisture transfer model 3.21:

$$\rho_l \Phi\left(1 - \frac{\rho_v}{\rho_l}\right) \frac{\partial S_l}{\partial h} \frac{\partial h}{\partial t} = \operatorname{div}\left[\left(\frac{k_{la}}{h} \cdot \frac{\rho_l^2 R T}{\mu_l M_v} + D_{va} \cdot \frac{p_{vs} M_v}{R T}\right) \nabla h\right]$$
(3.21)

This is a non-linear partial differential equation, the saturation degree or relative humidity changes over time and space. Besides, the apparent permeability of liquid k_{la} is a positive correlation function of relative humidity h:

$$k_{la} = f(h)$$

and the apparent diffusivity of vapor D_{va} is also a function of relative humidity h:

$$D_{va} = f(h)$$

Physically speaking, if relative humidity increases, the pore networks are more filled with water and the liquid pathway is increasingly continuous, which is positive to the transfer of water in liquid phase. That is to say, in high relative humidity domain, the liquid water transfer contribute the most part in water transfer phenomenon. In contrary, if the relative humidity decreases, more and more porous space are filled with vapor, namely less connection between liquid water, leaving more space for the air vapor to pass through. In this way, the diffusion of water vapor will dominate the water transfer process.

In this model, saturation degree is expressed by the driving force of relative humidity

h, it is also practical to transform to the driving potential of capillary pressure, by applying the Kelvin's law in Eq. 3.13. On this occasion, the moisture transfer model will be equation 3.22.

$$\rho_l \Phi \left(1 - \frac{\rho_v}{\rho_l} \right) \frac{\partial S_l}{\partial p_c} \frac{\partial p_c}{\partial t} + \mathbf{div} \left[\left(k_{la} \frac{\rho_l}{\mu_l} + D_{va} \frac{p_{vs}}{\rho_l} \left(\frac{M_v}{R T} \right)^2 e^{-\frac{p_c}{\rho_l} \frac{M_v}{R T}} \right) \nabla p_c \right] = 0$$
(3.22)

It is worth noting that in the establishing protocol of the moisture transfer model, the two phenomena (permeation of liquid and diffusion of vapor) are considered independently. It is a transferring pattern of *parallel* style, which means each of them takes the displacement on its own local domain and no interaction with one and the other.

To calculate the model Eq. 3.21 in discrete equation, we need to relate the variable terms with regard to the independent variable (relative humidity h).

Firstly, the term $\frac{\partial S_l}{\partial h}$ on left-hand side of the model is the derivative of the water vapor sorption isotherms (WVSIs). The relationship between the degree of saturation and relative humidity is given by the van Genuchten equation [van Genuchten, 1980], as in Eq. 3.23.

$$S_{l} = \left[1 + (-b_{vg} \ln(h))^{\frac{1}{1-a_{vg}}}\right]^{-a_{vg}}$$
(3.23)

where a_{vg} and b_{vg} are two parameters that can be obtained by fitting experimental results of the desorption isotherm for the tested material.

Secondly, the two terms on the right-hand side k_{la} and D_{va} are related to the liquid permeability and water vapor diffusion, respectively. Both of them are function of relative humidity, as already mentioned in the previous section.

As defined in Eq. 3.8, the apparent permeability of liquid k_{la} is expressed by:

$$k_{la} = k_{rl} \ K_0$$

In which, K_0 is the intrinsic permeability, as introduced previously in Eq. 3.7. k_{rl} is the relative permeability. This term can be determined by the Mualem empirical relationship [Mualem, 1976], shown in Eq. 3.24.

$$k_{rl} = S_l^{p_{krl}} \left[1 - \left(1 - S_l^{\frac{1}{a_{vg}}} \right)^{a_{vg}} \right]^2$$
(3.24)

where S_l is the saturation degree, p_{krl} is a fitting parameter.

At last, there is the apparent vapor diffusivity D_{va} to be transformed. In the same way, the diffusion of water vapor is highly dependent on the saturation degree. In addition, the tortuosity of the concrete porosity also influences this parameter. An empirical model was developed to take both parameters into account [Millington and Quirk, 1961]. The relationship is given by the empirical Millington and Quirk equation [Millington and Quirk, 1961], as expressed in Eq. 3.25.

$$D_{va} = D_0 \,\,\Phi^{amq} (1 - S_l)^{b_{mq}} \tag{3.25}$$

Therefore, D_{va} is related to the degree of saturation, the porosity, and the intrinsic diffusion coefficient of water in air D_0 .

It is worth noting that the Milington and Quirk equation is just empirical formula, so does the Mualem equation. The function curves could cover a big part of the window by adopting different fitting coefficients. Therefore optimization of parameters are necessary. Since if the constitutive equations are not correct, it will change the results, but not the global methodology.

This is a simplified approach to establish the model, but not necessarily close to the real situation. It is possible that at some local position, these two mechanisms behave in *series* style, like one following the other. It is interesting to quantify the two different patterns and figure out how this affects the moisture transfer process, which will be discussed in the following Chapter 4.

3.2 Numerical simulation with CAST3M

The model described above is implemented in the finite element software CAST3M. The geometries are meshed with discretization along the water transfer direction (x axis). In the simulation program, we consider a one-dimensional problem because our goal is to identify material parameters by using an iterative algorithm. Three-dimensional calculations in CASTEM is also possible, but quite time-consuming. For identification of parameters and capturing the main physics, it is more practical and efficient to perform the calculation in 1D.

The RH value is calculated as the average value of the elements related to probe

scale in the drying direction (diameter of 5 mm) for the corresponding sensors. Fig. 3.1 gives an example of meshing and with humidity sensors. The mass loss value is an integral of water content over the entire domain at any time point.

Due to the fact that the drying gradient is greater in the position that is close to the surface than the inner part of the samples, the meshing in x direction is irregular mesh. It is higher density close to the drying surface.

To solve Eq. 3.21, and related boundary condition, we compute using implicit approach, the term $\frac{\partial S_l}{\partial h}$ (Eq. 3.23), and estimate the apparent permeability (Eq. 3.24) and apparent diffusivity (Eq. 3.25).

In the beginning of the calculations, the used parameters for the model are extracted from the recommendations of the thesis [Hilaire, 2014].

In addition to initial values of parameters, the modeling of drying requires also the definition of adapted boundary conditions. It is one possible method to impose directly the ambient relative humidity at the air-concrete interface [Hilaire, 2014, Oxfall et al., 2016]. However, such methodology doesn't take into account the exist of a boundary layer of air. At the air-concrete interface, the moisture content depends on the distance to the surface of concrete. This is important at the initial period of drying, because the high moisture content initially observed at the concrete surface gives rise to a boundary layer of air with high humidity at the air-concrete interface, which initially slows the drying kinetics [Carette et al., 2020].

$$J_{BC} = h_c \cdot (h_s - h_{ext}) \tag{3.26}$$



Figure 3.1: An example of meshing and sensors in prismatic samples

The thickness of this boundary layer strongly depends on the ambient conditions (air flow, temperature) and the material surface condition (surface roughness and moisture) [Zhang et al., 2015]. Such boundary conditions can be more accurately represented by Eq. 3.26, in which J_{BC} represents the flow of water vapor at the air-concrete external interface, h_s is the relative humidity at the interface and h_{ext} is the external air relative humidity. The value of h_c is not consistently defined and can reach values from 1×10^{-2} [Zhang et al., 2015] to 8×10^{-7} [Ozbolt et al., 2016] in natural conditions.

3.3 Optimization of experimental method based on parameters analysis

As previously illustrated in Chapter 2, we adopted the measurement of both mass loss and relative humidity to follow the drying process in concrete specimens. In parallel, a nonlinear diffusion-drying model containing liquid permeation and vapor diffusion in drying mechanism is applied to estimate the drying process.

For the experimental method, the difficulty relies to the time-consuming method to follow the slow drying phenomena, and also uncertainties and difficulties to trace the inner moisture profiles, resulting to the insufficient database for performing numerical calculation. For the simulation part, as the results depend highly on parameters which remain unfixed variables, is the optimization process based on the experimental data is necessary to identify the value of parameters, so as to verify the model.

In order to find out the adequate experimental data within the shortest time duration, and figure out the proper positions and sufficient quantity of sensors to detect relative humidity inside the concrete, we did calculation on optimization of parameters for different time duration windows and varied different sensor positions. An identification procedure for the parameters involved in the model was carried out based on Finite Element Modelling Updating method (FEMU) using CAST3M and MATLAB coupling. The previous obtained experimental results of drying in concrete is considered as database, with different geometries (cylinder and prismatic) during 162 days, following both mass loss and internal relative humidity at different positions.

The identification flow chart together with experiment and simulation framework is presented in Fig. 3.2. As it is illustrated, the protocol could be globally divided



Figure 3.2: Identification algorithm flow chart [Ma et al., 2020]

into three parts, which are indicated in three different background colors. The first is related to the experimental data obtained in this study; a second part presents the finite element simulation process, and the last part is associated with the minimization algorithm, developed in MATLAB.

3.3.1 Positions of humidity sensors

The geometries of the specimen are illustrated in Fig. 3.3. We take the samples from drying group, which are clarified in two different geometries: cylindrical shape for radius drying and prismatic for lateral drying on two opposite surfaces $(7 \times 7cm^2)$. All the other surfaces are tightly covered by aluminum, in order to guarantee the onedimensional drying. The dimension of each geometry and the positions of sensors are already illustrated in Section 2.3. In order to specify the position of each sensors, we named A B C to represent the name of sensor settled at different positions of the samples, as shown in Fig. 3.3. The internal relative humidity data are collected by the probes and mass loss of sample with the same shape is regularly recorded manually by weight balance. For the cylinder samples, two sensors are fixed at 1.5 cm and 5.5 cm to the drying surface, corresponding to position A and B; and for the prismatic samples, three sensors are fixed at the distance of 1.5 cm, 3.0 cm, and 6.0 cm to the drying surface, corresponding to position A, B and C, respectively.



Figure 3.3: Schematic diagram of sensors positions for the drying samples of two geometries

3.3.2 Levenberg-Marquart's minimization

In this study, an identification procedure based on experimental data of mass loss and humidity evolution for both the prismatic lateral drying and cylindrical radius drying for seven parameters in the model and equations mentioned above is performed. The identification procedure adopts Finite Element Modeling Updating method (FEMU) [Neggers et al., 2015] implemented in CAST3M and MATLAB. In the FEMU method, minimization of an error function is built based on the difference between experimental data and numerical results calculated from CAST3M. As shown previously in the flow chart Fig. 3.2, the experimental obtained data is compared with numerical results and finally the minimization algorithm is operated in MATLAB.

The methodology applied on both geometries, with the boundary condition: temperature of 38 °C, relative humidity of 32 % and for the test time duration of 16 days, 40 days, 80 days, 120 days and 160 days respectively. Iterations of comparison between numerical and experimental data leads to a set of optimized parameters for each test duration. The most comprehensive data results of each test group (either the longest time duration or the most humidity information included) are taken as the local reference, in order to have the profile of how parameters change over different window duration, and to figure out the most optimized methodology that is sufficient for precise modeling of drying process.

$$\overrightarrow{Error} = \sum_{Samples} \left[\frac{\overrightarrow{C}_{ML}^{e}}{max(\overrightarrow{C}_{ML}^{e})} - \frac{\overrightarrow{C}_{ML}^{s}}{max(\overrightarrow{C}_{ML}^{s})} \right] + \sum_{Sensors} \left[\frac{\overrightarrow{C}_{RH}^{e}}{max(100 - \overrightarrow{C}_{RH}^{e})} - \frac{\overrightarrow{C}_{RH}^{s}}{max(100 - \overrightarrow{C}_{RH}^{s})} \right]$$
(3.27)

This inverse modeling depends on a prior knowledge of the drying model and its accuracy to predict the drying process. The error function is given by Eq. 3.27, which includes experimental data indicated by the e exponent, and simulated data indicated by the s exponent, as well as results from mass loss measurements, which is indicated by the ML index and from relative humidity measurements indicated by the RH index. The max sign in the equation means the maximum value (either mass loss or relative humidity) in their corresponding group.

This function ensures that several samples or sensors for the same measurement can be included independently from one another in the identification process. Finally, using initial input parameters, the minimization is calculated based on Levenberg-Marquart's optimization method implemented in MATLAB. The Levenberg-Marquardt algorithm (LM) interpolates between the Gauss-Newton algorithm and the method of gradient descent. However, as with many fitting algorithms, it finds only a local minimum, which is not necessarily the global minimum. For information can be referred to [Moré, 1978, Pujol, 2007]. The framework of the algorithm is presented in Fig. 3.4.

The minimized parameters resulting from this process are entered in CAST3M as input parameters. The identification runs until it reaches a criterion based on the aver-

```
Algorithm 1: Levenberg-Marquardt resolution
  1 Input : Experimental points C_i^{exp}, \delta_{max};
 2 Arbitrary initialization \mathbf{p}_0
 3 begin
               \mathbf{k} \leftarrow 0;
 4
               \theta \leftarrow 10^{-3}:
  \mathbf{5}
               \mathbf{J} \leftarrow \frac{dC}{d\mathbf{p}_0};
 6
               \mathbf{p} \leftarrow \mathbf{p}_0;
 7
               while STOP-CRIT and (k < k_{max}) do
 8
                       k \leftarrow k+1;
 9
                       if \theta \equiv \sqrt{k} \pmod{2} then
10
                              Actualisation : \mathbf{J} \leftarrow \frac{dC}{d\mathbf{p}_k};
11
                      Get C_i^{sim}(\mathbf{p}) from simulation;

\mathbf{f} \leftarrow C_i^{exp} - C_i^{sim}(\mathbf{p});

\lambda \leftarrow \theta \|\mathbf{f}\| + (1 - \theta) \|\mathbf{J}^T \mathbf{f}\|
12
13
14
                       Find \boldsymbol{\delta} such that (\mathbf{J}^T \mathbf{J} \cdot \boldsymbol{\lambda} \ \mathbb{1}) \ \boldsymbol{\delta} = \mathbf{J}^T \mathbf{f};
15
                       if abs (\delta) \leq \delta_{max} then
16
                                \mathbf{p} \leftarrow \mathbf{p} + \boldsymbol{\delta}
17
                       else
\mathbf{18}
                              \mathbf{p} \leftarrow \mathbf{p} \pm \delta_{max}
19
```

Figure 3.4: Minimisation algorithm

age relative increment of the identified parameters increments. If this average variation remains below the limit of 0.3% of the current parameters values, the identification procedure is stopped. The main steps of the simulation program are presented as following:

- Update the experimental data for each geometry. With these updated parameters, CAST3M program runs to get the corresponding results, followed by the minimization calculation in MATLAB. Optimized parameters for each time duration window are obtained thereby.
- Test firstly only for mass loss of each geometry, followed by mass loss plus humidity data provided by one sensor, then add one more humidity information until all the collected data are applied in the optimization program.
- Taking the locally most comprehensive results as the reference set of parameters. This is to figure out how the other shorter windows or less humidity sensors conceive to the relative variation value of the parameters.
- In order to accelerate the calculation, every time of the input parameters takes

the value of latest optimized set of parameters. This allows less iterations to reach optimized new parameter value.

3.4 Results and discussion

The simulation results will be presented in two parts: first the mass loss and humidity profile for the prismatic lateral drying, followed by the numerical results of cylindrical radius drying.

3.4.1 Results for prismatic lateral drying

The experimental and numerical results of mass loss and relative humidity for prismatic concrete are presented in Fig. 3.5 and Fig. 3.6, respectively. The relative mass loss in Fig. 3.5 presents the linear diffusion tendency for lateral drying, and favorable fitting of experiment and numerical are obtained. The relative humidity results at three test points of prismatic sample are shown in Fig. 3.6, the test points is corresponding to 1.5 cm, 3.0 cm and 6.0 cm to drying surface.

In order to analyze the optimized parameters based on a time window method, different window duration are shown with the analysis duration of 16, 40, 80, 120 and 160 days. The test runs for each time window, which is represented by each square in different colors, with only mass loss data or both mass loss and relative humidity results, as shown in Fig. 3.5 and Fig. 3.6.

Taking the mass loss window analysis as an example, the optimized parameters for different time duration are listed in Table 3.1. In this case, the optimized parameters based on the longest duration (162 days) are taken as a reference group, and the relative variation of all other test durations with the reference are computed and results are shown in Fig. 3.8. In order to have a uniform comparison for all the calculation results, 5% of the relative variation is set as a criterion value, which is marked by y = 5% as shown by dashed line in Fig. 3.7 or in Fig. 3.8.

Fig. 3.7 shows the tendency of all the parameters in test of mass loss. It is obvious that three of those parameters keep a relative high level (more than 20 %) until 90 days, and after that, for a longer time duration, most of the parameters variation decrease rapidly to the reference value. However, in order to include all the parameters variation



Figure 3.5: Experimental and optimized simulation results of ML with illustration of time window method in prismatic lateral drying



Figure 3.6: Experimental and optimized simulation results of RH, with illustration of time window method in prismatic lateral drying

within the error of 5 %, a test duration of at least 150 days is required, and a semi logarithm axis plotting shows more apparently the tendency in Fig. 3.8. This indicates that in prismatic lateral drying, only mass loss data is not sufficient, the relative humidity value is required to obtain parameters within predefined errors. The results for mass loss with one and two relative humidity data are given by Fig. 3.9 and Fig. 3.10,



Figure 3.7: Relative variation of parameters versus time duration based ML for prismatic lateral drying



Figure 3.8: Relative variation of parameters versus time duration based ML for prismatic lateral drying (semi-logarithm coordinate)

respectively.

In comparison with the test results with only mass loss, Fig. 3.9 indicates that if one sensor is added in addition to mass loss, the criteria relative variation of 5 % to reference

Identified	Test duration (days)				
parameters	16	40	80	120	160
p_{krl}	0.87019	0.87199	0.8687	0.85738	0.84892
$K_0(10^{-21})$	8.07	8.04	7.97	7.24	6.20
a_{mq}	2.5935	2.6047	2.5566	2.3899	2.1137
b_{mq}	0.740	0.740	0.739	0.734	0.722
a_{vg}	0.24907	0.24842	0.24643	0.21337	0.17161
b_{vg}	0.22387	0.21819	0.22052	0.23016	0.2331
$h_c(10^{-5})$	9.00	9.02	9.00	8.93	8.87

Table 3.1: Optimized parameters value for prismatic with mass loss data



Figure 3.9: Relative variation of parameters versus time duration based on ML with one RH at position A and for prismatic

value will be reached at about 100 days, instead of 150 days. Moreover, the relative humidity data also contribute to determining parameters, which is positive in improving precision of simulation humidity profile, instead of only precision guaranteed in mass loss. Therefore, the inner humidity data is necessary to supply for precision prediction of drying modeling and it contributes to save considerable time for the experimental duration.

Results of prismatic geometry test with data of mass loss and two relative humidity value at $1.5 \ cm$ and $3.0 \ cm$ to the surface are presented in Fig. 3.10. It is obvious that until the duration time of 80 days, the relative error has already reached a low



Figure 3.10: Relative variation of parameters versus time duration based on ML with two RH points at position A and B for prismatic

value of 2 %, which is less than half of the pre-defined critical error of 5 %. If there are two measure points for relative humidity with mass loss test, the time duration to reach relative variation error of 5 % will decrease to around 70 days. In comparison with results of only one sensor, which takes the measurement time of 100 days to reach the same relative error level, a second sensor data will contribute to reducing 30 % of experimental test time to reach the same level of relative error, and more than 50 % of time in comparison to test with only mass loss.

In order to analyze the effect of sensor numbers and positions, we took the identified parameters based on mass loss and three humidity points for a test duration of 160 days as a reference for the relative variation of parameters for different sensor numbers and position combinations. Absolute results are plotted in Fig. 3.11 in histogram and every color represents one parameter. The x-axis shows the name and combinations of the sensors in the prismatic geometry as previously shown in Fig. 3.3.

According to results in Fig. 3.11, it shows globally that more sensors are better than less because of a generally lower variation error. If there is only one sensor applied, represented by A, B or C, we found that the position A, which is closest to the drying surface, is better than the other two. This is probably due to the higher gradient of humidity when probe is closer to the interface exposed to external environment. In addition to this sensor A, add any one more sensor will also slightly improve the precision.



Figure 3.11: Effect of sensor numbers and positions on relative variation of parameters for prismatic case

Results between zero sensor and one sensor represented by C or B, suggested that only one sensor at the far position from drying surface does not contribute to the precision of the parameters, it could also be worse than no sensors, meaning larger relative variation. This can be explained that for the further distance to the drying surface, the relative humidity change so slowly and even keep constant at high value that it doesn't provide any practical information of the inner humidity profile, and the parameters goes further from the real one to fit with the experimental data.

However, it is noteworthy that the simulation and identification process is highly dependent on the precision of the tested experimental data, and for the experimental data, the most comprehensive information for humidity is captured by position A, which is the closest to the lateral drying surface.

Making a comparison between A and BC, we can also discover that it is not necessary the more sensors the better to contribute to the precision of the results, but also the position of the sensors for relative humidity measurement is very important. The relative variation error is within 5% or the sensors of A and combination of AC or AB, namely if two sensors are applied for humidity measurement, the combination of two sensors has to include the one which is most close to the drying surface, otherwise two sensors is no better than one.

3.4.2 Results for cylindrical radius drying

The experimental and simulation results for cylinder geometry test of mass loss and relative humidity for two probes are presented in Fig. 3.12 and Fig. 3.13, respectively. The same calculation method with prismatic case is applied to analyze the cylinder radius drying case.



Figure 3.12: Experimental and optimized simulation results of ML for cylinder radius drying

Fig. 3.12 shows obviously that the mass loss evolution is not linear to square root of time any more, but a higher drying rate at the beginning and slow down afterward, for the reason that the surface area is not constant along the moisture transport direction for the cylindrical radius drying.

The parameters resulted from longest test duration of 162 days is taken as the reference value, relative variation of parameters for the test of only mass loss is plotted in normal axis Fig. 3.14, and in semi-logarithm axis Fig. 3.15. It presents in Fig. 3.14 that



Figure 3.13: Experimental and optimized simulation results of RH for cylinder radius drying



Figure 3.14: Relative variation of parameters versus time duration based on ML results

for all the parameters, with increasing the tested time duration windows, tendency of relative variation is decreasing and getting closer to the reference value. It also indicated that the time duration of at least 140 days is necessary to reach a criteria error within



Figure 3.15: Relative variation of parameters versus time duration based on ML results (semi-logarithm coordinate)

0.05, on condition that the test data is performed only on mass loss.

Fig. 3.15 is the results re-plotted in logarithm axis, it shows that except the parameter b_{mq} , all the other parameters roughly follow the linear tendency, which represent an exponential evolution of continuously decreasing and infinitely reaching close to asymptotic line.

For the parameter b_{mq} , which is the index in Millington and Quirk equation, the tendency is not so regular, but for all the value, the relative change is below 1 %, which is almost negligible in variations. Therefore, it could be considered already to reach the relative real value with the reference value. Results of relative variation for mass loss and one humidity sensor data at position B, which is 1.5 cm to the surface are shown in Fig. 3.16 and Fig. 3.17.

It is indicated that all the parameters getting closer and closer to the reference value, which shows similar tendency with test only with mass loss. The gradient is high until approaching 80 days, the rate decreases afterwards. This indicates that 90 days can be considered as a criteria that all the parameters relative variation are included within a criteria error of 0.05. This is deduced around 50 days in comparison with the results of only mass loss test, meaning that to reach the same level of relative error, 35 % of test



Figure 3.16: Relative variation of parameters versus time duration based on ML and RH point at position A for cylinder case



Figure 3.17: Relative variation of parameters versus time duration based on ML and RH point at position A for cylinder case (semi-logarithm coordinate)

time is saved if one humidity information is added to mass loss test.

The two parameters in Millington Quirk equation a_{mq} and b_{mq} , show some oscillation phenomena. Nevertheless, for these two parameters, the relative variations is much lower than the others for all the time duration, and both of them are below 1 % when time duration is more than 50 days.



Figure 3.18: Effect of sensor numbers and positions on relative variation of parameters for cylinder case

Comparing with the test results with only mass loss, we can conclude that if one sensor is added to the test of mass loss, the time duration of criteria relative variation of 0.05 to reference value will decrease from more than 140 days to 90 days. To express in another way, if the same time duration of 120 days is performed, the precision will increase from 5 % to 1 %. Therefore, that inner humidity data is necessary to supply for precision prediction of drying modeling and it helps to save considerable time for the experimental duration.

The set of parameters, which is deduced from of mass loss and all the relative humidity of cylinder drying fittings for 160 days, are taken as local reference for analyzing the number of sensors and positions effect on optimized parameters results. The relative variation of parameters for cylinder based on the number of sensors and different positions is shown in Fig. 3.18.

Taking the results of both sensors as reference value, we can see from the results that all the parameters except the intrinsic permeation k_0 show a decreasing tendency of relative variations with the increase of sensor test numbers. If there is no value of relative humidity, the relative error could be as large as 50 % for some high sensitivity parameters, as parameter used in relative permeation p_{krl} and parameter in van Genuchten equation a_{vg} . It also indicates that for the position of 1.5*cm* to the drying position is better than the position of 5.5 *cm*, since almost all the parameters gives less difference to the reference value. This is reasonable that the position, which is closer to the drying surface, is more necessary and useful because the higher gradient of humidity difference appears closer to the drying interface.

3.5 Conclusions

The deducing process and simulation method of the drying model is introduced in this chapter. Based on the computational method to calculate humidity and mass loss, this identification approach, an numerical-experiment-identification coupling method is proposed to predict drying phenomenon. Finally the prediction of the optical experimental methodology can be analyzed based on this coupling approach and different test duration.

A non-linear diffusion model concerning two phenomena of liquid water permeation and water vapor diffusion is used to predict the hydraulic state of concrete material. The identification procedure of parameter in the models is performed based on an in-house identification tool coupling MATLAB with CAST3M. Simulation results for each geometry with proper identified parameters show favorable fitting with experimental results.

Calculation on optimization of parameters for different time duration windows and available different sensor positions are analyzed to find out the adequate experimental data within the shortest time duration. Analysis of relative variation of parameters indicates that the precision of the calculation for parameters will increase with the measurement time duration of experiment, also with the addition information of the inner humidity evolution.

To be specific, for prismatic lateral drying, results of relative variation of parameters shows that it is necessary to have at least one sensor for inner relative humidity profile. The test duration time will decrease with the increase of humidity sensor numbers. A second sensor data will contribute to saving 30% of experimental test time to reach the same level of relative error, and more than 50% of time in comparison to test with only mass loss. If two sensors are applied for the humidity data, one of them has to be at the position that is close to the drying surface, in order to capture the faster variation under the high gradient of humidity.

For the cylinder radius drying, the relative variation of parameters follows roughly an exponential evolution of continuously decreasing to the reference value with the increase of test duration time, and the precision increases with the additional numbers of humidity sensor. There is around 50 test days shortening when there is one sensor information added in comparison with the results of only mass loss test. Two sensors are recommended for a higher precision of the calculation, and one of them has to be as close as possible to the drying surface. The closer position to the drying surface is better than the center positions, as almost all the parameters appear less difference to the reference value.

In short, to follow and predict the humidity profile inside concrete, the test of only mass loss is not sufficient to get precise parameters to apply in the drying model, at least one sensor information is necessary to predict the desorption profile. If only one sensor is applied in detecting the inner relative humidity evolution, the position, which is closer to the drying surface, is better than further ones. Nevertheless, in reality, it is also confined by the fixing technique of the sensors.

However, each parameter represents the some characteristics of the materials, surface condition, or boundary conditions, which are supposed to be the same for the same kind of materials and all the external environmental conditions are trying to be the same. The main differences between the two geometries are the type of drying, whether the surface areas is constant or not along the drying direction. Therefore, further discussion is needed on the physical meaning of the parameters to figure out the difference in the two results.

Chapter 4 Hypothesis discussion on the moisture transfer model

In this chapter, we will have a discussion on the hypothesis of the moisture transfer model. The model is characterized by a nonlinear diffusion coefficient, and it is valid based on some assumptions. These assumptions are adopted either to simplify the problem for easier calculation, or to approximate the real physics as close as possible. As porous material with complex structures, the modeling of moisture transfer relies much on the precision of the establishment of the model.

We underline that the chosen parameters or the identified set are related to the used samples, however a real variability does exist on the concrete. In a previous study of Issaadi [Issaadi et al., 2017], such spatial variability of transfer and storage properties (water porosity, water vapor permeability, intrinsic permeability and water vapor sorption isotherms) of a concrete were investigated as well.

There are mainly three parts are included in this chapter. In the first section, a simplified analytical solution with the hypothesis of linear coefficient in the drying model is proposed, based on the experimental results and optimization of parameters discussed in the previous chapters. It is a second order differential equation of diffusion analogy to thermal diffusion. In addition, the same approach is applied in the drying-imbibition cycles analysis. The difference lies in the modification of the boundary condition from constant value to oscillating function. This analogy method is adopted to figure out the physical process of moisture transfer problem with the thermal transfer problem. In this study, the target variable is relative humidity instead of temperature. The moisture transfer problem dealing with relative humidity, water displacement and moisture transfer is thereby in comparison to the heat transfer problem dealing with temperature and energy transfer.

In the second section, an analytical solution of the model dealing with the DI cycling results is proposed. The periodic 10 days of drying and 10 days of imbibition can be considered equivalent to oscillation boundary conditions in thermal transfer problem.

In the third section, we propose to discuss the moisture transfer pattern in the model, which means how the two phases (liquid and vapor) of water interact and influence the humidity profile and evolution inside samples.

The two phases of water in the model correspond to the two independent terms in the diffusion coefficient. The assumption focuses on the moisture transfer in a porous structure, and how the two controlling terms (diffusion of water vapor and permeation of liquid water) interact with each other. We make assumptions of what could be the coupling pattern of these two terms: do they interact more in parallel pattern, more in series pattern, or do they have a combined pattern of parallel and series? The latter pattern could be closer to the reality than the original model. Two cases of transfer pattern are considered, either the permeation of liquid water is in dominant position or both the permeation of liquid water and diffusion of water vapor are in the relative same order of magnitude. For each case, an interpolation factor is implanted to express the diffusion coefficient and the equivalent diffusion coefficient is calculated.

Results show that if the term of diffusion is negligible in comparison to the term of permeation, all the results of mass loss and relative humidity at different interpolation values can be unified by applying a dimensionless time. So the results of mass loss evolution and humidity evolution versus time could be predictable on any ratio contributions between parallel and series styles. On the other hand, if the two terms are relative same order of magnitude, no matter what the value of interpolation, consistent results of mass loss and relative humidity profile are obtained. In short, the parallel and series method supplies a possibility to analyze how the proportion of contribution of vapor and liquid affects the drying phenomena.

We didn't discuss about the case that the terms of vapor diffusion in predominant role, due to the fact that only in very low humidity level, the level of vapor diffusion could be competitive. As the analytical assumptions are based on our experiment results, which is mainly in the humidity range of 30 % to 100 %, the predominant driving force is more possible to be liquid permeation than vapor diffusion.

4.1 Simplified analytical solution for drying

Based on the experimental results and optimization of parameters discussed in the previous chapter, a simplified analytical solution with the hypothesis of linear coefficient in the drying model is proposed in this section.

An analogy method is adopted to figure out the similar physical process of drying phenomenon with the heat conduction phenomenon. The moisture transfer problem dealing with relative humidity and water content is therefore in comparison to the heat transfer problem dealing with temperature and energy transferred. In our problem, the target variable is relative humidity, instead of temperature.

4.1.1 Analogy between moisture and heat transfer problem

In the drying process, we consider that it is one-dimensional moisture movement, the model can be expressed as Eq. 4.9. In comparison with the one dimensional heat conduction governing (Eq. 4.1), the following reasonable analogy analysis could be made.

$$\rho \ c_p \ \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(\lambda \ \frac{\partial T}{\partial x} \right)$$
(4.1)

Where ρ , c_p , and λ are the density $(kg \cdot m^{-3})$, specific heat capacity $(J \cdot kg^{-1}K^{-1})$ and thermal conductivity $(W \cdot m^{-1} \cdot K^{-1})$, respectively. In order to have an apparent comparision, we put here again the drying model.

$$\rho_l \left[\Phi \; \frac{\partial S_l}{\partial h} \left(1 - \frac{\rho_v}{\rho_l} \right) \right] \frac{\partial h}{\partial t} = \mathbf{div} \left[\left(k_{la} \frac{1}{h} \frac{\rho_l^2 RT}{\mu_l M_v} + D_{va} \frac{M_v p_{vs}}{RT} \right) \nabla h \right]$$

On condition that the thermal conductivity is homogeneous throughout the field and constant with time, Eq. 4.1 can be rewrite as the following simplified format Eq.4.2.

$$\frac{\partial T}{\partial t} = a \frac{\partial^2 T}{\partial x^2}$$

$$a = \frac{\lambda}{\rho c_p}$$
(4.2)

The target variable h(relative humidity) is in the same position as T (temperature),

that is to say, we consider the left-hand-side item $\Phi \frac{\partial S_l}{\partial h} \left(1 - \frac{\rho_v}{\rho_l}\right)$ as the specific heat c_p in the thermal equation, the right-hand-side item $\left(k_{la}\frac{1}{h}\frac{\rho_l^2 RT}{\mu_l M_v} + D_{va}\frac{M_v p_{vs}}{RT}\right)$ as the isotropic conductivity λ , and the liquid density ρ_l as the material density ρ in the thermal equation.

In order to solve the transient diffusion problem, proper boundary conditions and initial condition are necessary to describe the phenomena and then to deduce unique solution.

The drying experiments for both prismatic and cylinder geometries are performed under constant environment condition: temperature of 38 °C, relative humidity of 32 %. Specimens at the beginning of drying are considered full saturation, so initial condition can be set as saturated humidity and homogeneous distribution.

In comparison to the transient heat transfer problem, the boundary condition can be considered constant imposed temperature or convection on the surface. Accomplished with the drying model, theoretically, the analytical solution is available if diffusion coefficient for the material is constant throughout the drying process. The following text will introduce the analytical solution of one – dimensional transient heat conduction problem for both prismatic and cylinder case.

For prismatic geometry, the Cartesian coordinate should be applied in one direction, and for the cylinder sample, solution established on cylindrical coordinate. In practice, both of the geometries could be considered as one dimension problem, because all the other surfaces are tightly covered by aluminum, so no mass exchange happened on other surfaces.

• Prismatic case expressed in Cartesian coordinate:

The one - dimensional transient homogeneous heat conduction can be described as: a plate with the span of L; the initial temperature T_i ; one boundary insulated; the other boundary subjected to a convective heat flux condition with the surrounding environment at T_{∞} .

This problem is equivalent to the quenching of a slab with the span of 2L, with identical heat convection applied on the external boundaries (x = -L and x = L). The mathematical formulation of the problem is to find T(x,t), which is given by Eq.



Figure 4.1: Schematic diagram of heat conduction problem in prism

4.3, and the goal is to solve the temperature distribution versus time and space on x direction. A schematic diagram is drawn to help understand the process in Fig. 4.1.

$$\frac{\partial T(x,t)}{\partial t} = a \cdot \frac{\partial^2 T(x,t)}{\partial x^2}$$
(4.3)

With the boundary conditions:

at x = 0, $\frac{\partial T}{\partial x} = 0$; at x = L, $-\lambda \frac{\partial T}{\partial x} = h_c \times (T - T_{\infty})$;

and initial condition:

for all x, when $t = 0, T(x, 0) = T_i$. In which, a is the thermal diffusivity $(m^2 \cdot s^{-1}); \lambda$ is the thermal conductivity $(W \cdot m^{-1} \cdot K^{-1}); h_c$ is convective heat transfer coefficient $(W \cdot m^{-2} \cdot K^{-1}).$

By defining the dimensionless parameters:

$$X = \frac{x}{L}$$
$$\tau = \frac{a \cdot t}{L^2}$$

$$\theta\left(X,\tau\right) = \frac{T\left(x,t\right) - T_{\infty}}{T_{i} - T_{\infty}}$$

we obtain the dimensionless expression of governing equation:

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial X^2}$$

with the boundary conditions:

at X = 0, $\frac{\partial \theta}{\partial X} = 0$;

at X = 1, $\frac{\partial \theta}{\partial X} + Bi \cdot \theta = 0$; and initial conditions:

for $\tau = 0, \ 0 \le L \le 1, \theta = 1.$

In addition, the definition of Bi is presented as Eq. 4.4.

$$Bi = \frac{h_c \ L}{\lambda} \tag{4.4}$$

Different Bi numbers represent different boundary conditions. When Bi number tends to infinity (in practice, generally Bi > 100), the boundary condition can be considered as imposed constant value. In contrast, when it is a finite value (lower than 0.1), it is considered as convection boundary condition with relative same order of convection coefficient and thermal conductivity.

• Cylindrical case expressed in Cylinder coordinate:

One - dimensional transient homogeneous heat conduction in a solid cylinder can be defied as: the radius b; the initial temperature T_i ; the radius surface is exposed to the surrounding environment at temperature T_{∞} and convective heat flux is imposed on the surface. A simple schematic diagram is shown in Fig. 4.2. The governing equation of this problem is expressed in Eq. 4.5:



Figure 4.2: Schematic diagram of heat conduction problem in cylinder

$$\frac{\partial T}{\partial t} = a \cdot \frac{1}{r} \frac{\partial}{\partial r} \left(r \cdot \frac{\partial T}{\partial r} \right) \tag{4.5}$$

with the boundary conditions:

at r = 0, $\frac{\partial T}{\partial r} = 0$; at r = b, $-\lambda \frac{\partial T}{\partial r} = h_c \times (T - T_{\infty})$.

By similar transformation with prismatic case to dimensionless expression, the following equation will be obtained.

$$R = \frac{r}{b}$$
$$\tau = \frac{a \cdot t}{b^2}$$
$$\theta \left(X, \tau \right) = \frac{T \left(r, t \right) - T_{\infty}}{T_i - T_{\infty}}$$

Thereby we induce:

$$\frac{\partial T}{\tau} = \frac{1}{R} \frac{\partial}{\partial R} \left(R \frac{\partial T}{\partial R} \right)$$

with the boundary conditions:

at R = 0, $\frac{\partial \theta}{\partial R} = 0$; at R = 1, $\frac{\partial \theta}{\partial R} + Bi \cdot \theta = 0$; and initial conditions: for $\tau = 0$, $0 \le R \le 1$, $\theta = 1$.

When the thermal diffusivity is constant, the analytical solution is available for one dimensional transient heat conduction problem. It is solved either by Laplace transform or separation of variables. According to the boundary condition and material properties, the analytical solution can be achieved for both cylindrical and Cartesian coordinate.

The solution based on series is expressed using the eigenvalues values vector λ_n obtained as solution of the transcendental polynomial given below (related to the boundary condition):

$$\theta = \sum_{n=1}^{\infty} \frac{4\sin\lambda_n}{2\lambda_n + \sin(2\lambda_n)} e^{-\lambda_n^2 \tau} \cos\left(\lambda_n \cdot X\right)$$
(4.6)

$$\lambda_n \tan \lambda_n = Bi$$

$$\theta = \sum_{n=1}^{\infty} \frac{2}{\lambda_n} \frac{J_1(\lambda_n)}{J_0^2(\lambda_n) + J_1^2(\lambda_n)} e^{-\lambda_n^2 \tau} \cos\left(\lambda_n \cdot R\right)$$
(4.7)

$$\lambda_n \frac{J_1(\lambda_n)}{J_0(\lambda_n)} = Bi$$

4.1.2 Results of dimensionless analytical solution

Eq. 4.6 is the analytical solution for one - dimensional transient conduction in a plane wall of thickness 2L, and both surfaces are subjected to convection. Eq. 4.7 is cylinder of radius r_0 subjected to convection from the circular surfaces.



c) Prismatic_Bi =200

d) Cylindrical _Bi =200

Figure 4.3: Analytical dimensionless RH profile vs. dimensionless time (z) and space (r)

The analytical solutions are calculated and plotted in Maple 12 software. Figure

4.3 indicates all the results for the two geometries with Bi number equals 50 and 200. Analytical solution for internal relative humidity versus time and space are plotted in 3D coordinate system. The r axis represents the relative scale in drying direction, and the z axis represents the time. It shows visually that for the cylindrical radius drying, humidity evolves faster than prismatic lateral drying, and the boundary turbulent effects further distance at the same time point.

Comparing the two cases with different Bi number in the same geometry, we can see the relative coherent trend, which indicates that the results is not sensitive to the boundary conditions. We will take the result from Bi = 50 for further discussion.

In order to compare the analytical result with numerical result performed in CAST3M, three positions of the humidity value are exported. The length 1.5 *cm* represents the distance to the drying surface. The analytical dimensionless humidity evolution for prism and cylinder are presented in Fig. 4.4 and Fig. 4.5, respectively.



Figure 4.4: Dimensionless RH evolution at different distances to drying surface for prism

One needs to draw attention in the transform, because the different positions in the specimen are described by the distance to drying surface, but x or r in the governing equations represent the distance from the 0 position, which is the center of the geometry. For prismatic, the three positions to the drying surface are 1.5 cm, 3.0 cm and 6.0 cm, corresponding to 0.893, 0.786, and 0.571 in dimensionless expression. The same transformation for cylindrical drying, the two positions 1.5 cm and 3.0 cm to drying


Figure 4.5: Dimensionless RH evolution at different distances to drying surface for cylinder

surface are corresponding to 0.727 and 0.0 in dimensionless length positions.

4.1.3 Validation of dimensionless transformation

In order to verify the dimensionless method, we use the constant coefficient estimated above and apply these values in CAST3M, absolute results of relative humidity versus time is obtained and transformed to dimensionless by the following expressions:

$$RH = \frac{h - h_{ext}}{h_0 - h_{ext}}$$
$$\tau = \frac{t}{t_{ref}}$$
$$X = \frac{x}{L}$$

The defined parameters (RH, τ , X) represent the corresponding dimensionless values. h_0 is the initial relative humidity profile in field, as it is considered fully saturated at beginning of drying, $h_0 = 1$.

 h_{ext} is the external humidity, which equals 32 % in our experimental ambient condition and keeps constant.

L is the characteristic length for each geometry, which is half of the total drying length for prismatic (14 cm), and the radius value for cylinder sample (5.5 cm).

 t_{ref} is the reference time to transform time into dimensionless. In thermal equations, the expression is expressed as:

$$t_{ref} = L^2/a$$

In which, a is an equivalent diffusion coefficient, as expressed in Eq. 4.2. Due to the fact that diffusion coefficient is function of humidity, the reference time is dependent on the precision of estimated value of diffusion coefficient.

Feasibility is verified for this dimensionless method in Fig. 4.6 and Fig. 4.7. They present the relative humidity results of analytical solution and simulation results calculated in CAST3M with constant coefficient in the model. It indicates that for the cylindrical drying, the analytical method shows a relatively good fitting with simulation results, for both the two positions; while for lateral drying, it is less strictly fitted but within the error of 5 %, which is satisfactory in our study. In addition, the visual fitting aggregement is also enhanced when the time covers a larger scale.



Figure 4.6: Comparison of the analytical dimensionless RH with simulation results calculated with constant coefficient at different positions for prismatic

From the results above, we come to the conclusion that a validation was done between the simulation with linear coefficient problem and the analytical solution for both the cylindrical and prismatic case. However the present problem exhibits a non constant coefficient which are strongly dependent on the local water contents. The second complicate phenomenon concerns the antagonist change in the two diffusion contribution with the increase of humidity. We will explore and quantify such contribution in the



Figure 4.7: Comparison of analytical dimensionless RH with simulation results calculated with constant coefficient at different positions for cylinder

next section.

4.1.4 Comparison of analytical and nonlinear simulation results

From a perspective of the key parameters, the equivalent diffusion coefficient D_{eq} and equivalent of heat capacity C_{eq} are dependent on the saturation degree, which means function of local relative humidity. Meanwhile, if we draw the profile of D_{eq} (Fig. 4.8) based on the simulation results of optimized parameters, we found that during a large humidity range, the equivalent diffusion coefficient does not change harshly. Therefore, it is reasonable to take an average value between a certain humidity ranges, or take an integral average value of the whole humidity range. For the equivalent of heat capacity term C_{eq} (Fig. 4.9), the constant range is not so obvious, so we take the integral of the whole humidity range from 32 to 100 percent, which is the gap between the initial humidity and ambient humidity. The parameters evolution and the average value for both the geometries are shown in Fig. 4.8 and Fig. 4.9, respectively.

For the equivalent conductivity D_{eq} , if the same integral approach is applied to get the average value, the results will be overestimated. This is mainly due to the high nonlinearity of the equivalent conductivity profile at the relative high humidity region. It shows in Fig. 4.8 that for the lower humidity (less than 50%) and near saturated region, the value could be difference of two orders of magnitude. This also can be illustrated



Figure 4.8: Equivalent diffusion term and estimated value for prismatic and cylinder

from the nonlinear diffusion equation that when coefficient is function of variables, in addition to the $a \cdot \nabla^2 h$ term, there is also another term $f \cdot \nabla h$ affecting the results. So here the estimated value are lower than average.



Figure 4.9: Equivalent of heat capacity and estimated value for prismatic and cylinder

Therefore, the equivalent diffusion coefficient can be obtained, as well as the calculated reference time based on the value of estimated parameters. The summary of all the calculated values are listed in Table 4.1 (D1, D2 represent prism and cylinder, respectively).

For the numerical result, humidity at all the positions starts to decrease in the begin-

Sample	$C_{eq}[10^{-2}]$	$D_{eq}[10^{-8}]$	$a_{eq}[10^{-10}](m^2/s)$	$t_{ref}[10^2](day)$	L(m)
D1	9.80	1.25	1.27	17.8	0.14
D2	12.7	1.66	1.31	2.67	0.055

Table 4.1: Summary of parameters in analytical solution

ning of drying process, but with different ratios. For the analytical solution, humidity at the closer position to drying surface starts to decrease immediately, and humidity at the inner positions has a relative horizontal region before it begins to decrease. This is more obvious when plotted in shorter time duration.

By applying the same non-dimensionalization procedure to the non-linear simulation results of relative humidity versus time in dimensionless expression for both the two kinds of drying patterns, we obtain the results in Fig. 4.10 and Fig. 4.11.



Figure 4.10: Comparison of the analytical solution and non-linear simulation results for RH for prismatic sample

The results indicate that for both the lateral and radius drying patterns, the simplified analytical solution could supply favorable fitting for humidity profile when the position is close to the drying surface (1.5 cm, 3.0 cm to drying surface for prismatic and 1.5 cm to drying surface for cylindrical drying). However, for the relative center position or positions that are far from the drying surface (6.0 cm to drying surface for prismatic and 5.5 cm to drying surface for cylinder), the difference between analytical solution and non-linear simulation results is much larger, and the difference decreases



Figure 4.11: Comparison of the analytical solution and the non-linear simulation results of RH for cylindrical sample

with the drying process going on.

4.2 Simplified analytical solution for drying-imbibition

In this section, an analytical solution of the model dealing with the DI cycling results are proposed. The periodic 10 days of drying and 10 days of imbibition can be considered equivalent to the oscillation boundary conditions in the thermal transfer problem.

To recall the experimental content in Chapter 2, we have two drying-imbibition conditions:

- In the first case, the drying environment condition is 25 °C and 45 % and the imbibition process is at the same temperature and the samples are in water contact.
- In the second case the drying environment condition is 38 °C and 32 % *RH* and the imbibition is at temperature of 25 °C and the samples are in water contact.

The two ambient conditions in DI experiments are plotted on the humid air diagram shown in Fig. 4.12.

The first test involves mainly the humidity potential for drying and during imbibition (black arrow in Fig. 4.12). The second test couples the two phenomena of the humidity effect for drying and the temperature change on the sample over time (red arrow in



Figure 4.12: Humid air diagram marking the two conditions in DI test

Fig. 4.12). This means that the temperature and the humidity change over time on the sample. The involved physics is more complex because the change in temperature over time will affect the humidity level and the equilibrium on the local interfaces.

Such effect will induce inner evaporation or condensation. The change in temperature will induce complex coupling on adsorption consequence of such change of temperature. We have to mention also that for this problem we try to keep mono-dimensional, however the temperature change on the sample will be bi- to tri-dimensional because the samples were not enough thermally insulated .

For diffusion problem in semi-infinity domain, we have the previous defined governing Eq. 4.2, which is:

$$\frac{\partial T}{\partial t} = a \ \frac{\partial^2 \ T}{\partial \ x^2}$$

At x = 0, we impose:

$$T(0,t) = T_0 + \Delta T \times \cos(\omega \cdot t)$$

where $\omega = \frac{2\pi}{\varsigma}$ is the pulsation, and ς is the period and corresponds to 20 days in the present study.

This approach using sinusoidal boundary condition is adopted just for illustration

because the considered problem is different: the boundary condition changes instantaneously and maintains on half cycle, which is illustrated in Fig. 4.13.

The other difference is that the imbibition is in direct contact with water so the capillary suction on the external face is activating, and it could be different from the boundary condition of saturating ambiance (RH close to100 %). The model used and some works shows that the two conditions are equivalent in curing concrete and conservation. However, in the present cycling problem the direct water contact will avoid the air displacement and constraint more the phenomena after the first capillary imbibition.



Figure 4.13: Illustration between sinusoidal external condition and square condition

The solution for the sinusoidal case is:

$$T(x,t) = T_0 + A_0 \ e^{-\sqrt{\frac{\omega}{2a}} \cdot x} \cdot \cos\left[\omega \ t - \sqrt{\frac{\omega}{2a}} \ x\right]$$

In which, $\sqrt{\frac{\omega}{2a}} x$ is the delay (increasing with x), $e^{-\sqrt{\frac{\omega}{2a}}}$ is the damping coefficient, and $A_0 e^{-\sqrt{\frac{\omega}{2a}} \cdot x}$ is the damping function.

The analytical solution for this problem is given in 3D coordinate system, presenting the humidity (or temperature) profile versus time and space, as shown in Fig. 4.14.

If we analyze the total energy in the domain, correspondingly it is equivalent to the



Figure 4.14: Analytical solution for DI periodic boundary (humidity or temperature profile) vs. time and space

mass contain in moisture field. The expression is given by Eq. 4.8:

$$Energy(t) \sim \int_{x=0}^{x \to \infty} T(x, t) dx$$
(4.8)

And it's obvious that it will keep the same frequency evolution and it will oscillate around the two extreme boundary conditions, *i.e.* fully saturated (100 %) and at fixed lower boundary condition (45 % or 32 %). The asymptotic oscillation of the total energy will be the average state corrected by the change over time on the damping area $(e^{-\frac{x}{x_{skin}}})$. Such damping area is the skin effects mainly controlled by the equivalent diffusivity and the frequency.

$$x_{skin} = \sqrt{\frac{2a}{\omega}}$$

The experimental results discussed before are plotted with mainly the damping behavior obtained by the evolution over time of the maximum gained and lost water on the consecutive cycles (see Fig. 4.15 and Fig. 4.16). The different environment condition is the drying ambient (for Fig. 4.15, it is 25 °C, 45 % RH; for Fig. 4.16, it is 38 °C, 32 % RH).

The two represented tests exhibit the damping phenomena over time of the maximum water gained and maximum water lost. The tenancy toward the average state with



Figure 4.15: Analytical fitting of mass variation in DI cycling for 25°C, 45 %~RH



Figure 4.16: Analytical fitting of mass variation in DI cycling for 38° C, 32 % RH

oscillation of water change are related to the skin region (represented by the mass relative variation amplitude). We plotted on the same figure a damped oscillatory analytical evolution, which is discussed previously in order to sketch up the occurring phenomena.

It is indicated in the two figures that the first and second cases exhibit a mass relative oscillation in the asymptotic domain with an amplitude of 0.32/2 and 0.48/2 respectively.

The applied conditions (RH, T) were illustrated in Fig. 4.12, and we can see that the limit variation of the specific humidity (vertical green axis, g water /kg dry air) are 8 and 12 (g water kg dry air) for the first and second test, respectively. If we have the same applied frequency (20 days) and same equivalent diffusivity, we will obtain the same skin effect scale. Therefore, under same porosity the induced ratio of water loss and water gained will be related to the change of the boundary conditions on water contain in air. Our two results confirm this correlated effect and exhibit the same order of magnitude (0.48/0.32 vs. 12/8). The two fractions are the ratio between the oscillating water change of the material and the water contain difference imposed on the boundary conditions, respectively.

This section analyzes the obtained results on the cycling of drying-imbibition and explains the observed tendency. What makes the phenomenon more complex is that the evolution don't exhibit symmetrical behaviors between drying and imbibiton processes. Such difference confirm the question on the limitation of the unique model to simulate accurately the two behaviors. Nevertheless, by applying the analytical approach, we achieved to obtain the results, explain and quantify the mechanism on such materials.

The presented results related to the humid air diagram allows to analyze the possible change over time, the asymptotic average value and the observed dynamics. The presented results are enough to predict qualitatively but not quantitatively, however it helps to know the dynamics of what is happening in order to choose the good sensor in future studies and also to know a prior the adequate locations of those used probes.

4.3 Model assumption of two phases interactions

In this section, we will have a discussion of moisture transfer pattern in the drying model, meaning how the two phases of water interact and influence the humidity profile and evolution. The two phases are the liquid and vapor of water, corresponding to the two terms of diffusion coefficient in Eq. 4.9.

$$\rho_l \Phi \; \frac{\partial S_l}{\partial h} \left(1 - \frac{\rho_v}{\rho_l} \right) \frac{\partial h}{\partial t} = \mathbf{div} \left[\left(k_{la} \frac{\rho_l^2 RT}{h\mu_l M_v} + D_{va} \frac{M_v p_{vs}}{RT} \right) \nabla h \right] \tag{4.9}$$

4.3.1 Parallel-Series model assumptions

The moisture transfer model in this study adopts several assumptions. One of the most important assumptions is that moisture transfer is considered in two forms: permeation of liquid water and diffusion of water vapor, and each of them takes the displacement on its own local domain. We name it *parallel* pattern, and there is no interaction with one and the other.

The consideration of the parallel pattern and without air movement could be limited in several situations. Some researchers in unsaturated cement-based materials under saline environment (chloride evolution) proposed more complex models taking into account the diffusion, the convection by moisture transport, the electrostatic coupling between ions and the chemical interactions through linear and non-linear isotherms [Sleiman et al., 2012]. A simplified experiment performing and analyzing the interlink connection among porous structures could refer to [Ma and Bennacer, 2019].

The assumption we adopted in this work is a simplified approach to establish the model, but it is not necessarily the reality. It is possible that at some local position, these two mechanisms behave in *series* style, like one following the other. It is interesting to quantify the two different patterns and figure out how it affects the moisture transfer process, which will be discussed below. Nevertheless, the physic will be more complex where product deposition occurs on the triple line (liquid-gas-solid connections), the nano- and micro-particles and the dissolved product will modify the interface properties [Li et al., 2018]. We don't take into account such complexity in this study.

Seen from Eq. 4.9, the right-hand side represents the moisture distribution on the domain, in which two mechanisms are considered: they are water vapor diffusion through the void and liquid water permeation along the capillaries. The controlling diffusion terms are $k_{la} \frac{h\rho_l^2 RT}{\mu_l M_v}$ and $D_{va} \frac{M_v p_{vs}}{RT}$, which are marked as D_c and K_c , respectively.

Analogy method is used to understand and modify the model. Here in the model, we consider that the two phenomenon control the drying process in parallel way (the two flux vector were added directly one to the other), which means the total flux is one plus the other, and they contribute to the drying process independently, shown as Fig. 4.17. The subscript p, s represents parallel and series, and l, v represent liquid or vapor.

In physical point of view, it means that the path of water vapor and the displacement



Figure 4.17: Schematic diagram of transfer resistance in parallel and series way [Ma et al., 2018b]

path of liquid water are independent and no interactions between each other. However, as the inner structure is complex, it is also possible that several layers of liquid water appear in the pore structure and vapor among them. In such case, the moisture transport could behave as in series way owing to the two phenomena interaction. In reality, the most possible situation is that both of the two transport patterns contribute to the moisture transfer process with some ratio.

However, it is difficult to know exactly the ratio between the two terms. Therefore we apply the interpolation factor n_{int} to express the equivalent diffusion coefficient (D_{eq}) . The goal is to estimate the two terms' contribution ratio. By updating the coefficient value in the model, we will calculate and find out how the two phenomena affect the results of mass loss and relative humidity evolution. As illustrated in Fig. 4.17, in a fixed domain, the resistance of a single phase in parallel way is four times of that in series way. Therefore, the expression of equivalent diffusion coefficient will be Eq. 4.10.

$$D_{eq} = n_{int} \times (D_c + K_c) + 4 \times (1 - n_{int}) \times \left(\frac{1}{D_c} + \frac{1}{K_c}\right)^{-1}$$
(4.10)

The used expression allows to pass from fully serial pattern to fully parallel pattern. The mixing between the two of any ratio can be expressed by using the interpolation factor n_{int} .

4.3.2 The case of permeation dominating

In case of $n_{int} = 1$, it is the original term in the model, the profile of equivalent diffusion coefficient and both D_c , K_c are shown in Fig. 4.18. It is worth noticing that the value of each term is highly depended on the parameters we choose. These parameters are chosen based on previous work [Carette et al., 2020], a set of optimized values that fit well with the experimental results on both mass loss and relative humidity.



Figure 4.18: Two contributions in diffusion coefficient profile (parallel case, n = 1)

Fig. 4.18 shows that in comparison with liquid permeation, the contribution of vapor diffusion is much smaller. Then we modify equivalent diffusion coefficient based on different interpolation values to cover from 0 to 1. The tendency of the profile is moving from completely parallel style $(n_{int} = 1)$ to series style $(n_{int} = 0)$ when interpolation value changing from 1 to 0, which is shown in Fig. 4.19.

It suggests a strong effect of the considered model on the equivalent coefficient controlling the drying process. The effect is both on the level and the tendency with a sudden decrease and increase of the coefficient in the vicinity of the humidity boundaries.

It is indicated also that with the decrease of interpolation value, the equivalent diffusion coefficient decrease in relative lateral way, which will induce a weaker and weaker ability in moisture transfer. As a result, a smaller and smaller mass loss value appears in the whole domain (see Fig. 4.20). Simulation results of relative humidity



Figure 4.19: Equivalent diffusion coefficient profile with different interpolation values for the permeation dominating case [Ma et al., 2018a]

in Fig. 4.21 also shows similar tendency for relative humidity at a fixed point which is $1.5 \ cm$ to the drying surface.



Figure 4.20: Simulation result of ML with different interpolation values

From Eq. 4.10, if we extract the interpolation factor and rewrite the equivalent diffusion coefficient in the form of the following equation, n_{int} is thus treated as variables with parameters A and B, which are function of relative humidity of the local position



Figure 4.21: Simulation result of RH with different interpolation values

and function of time.

$$D_{eq} = n_{int} \times A + B$$

We will have:

$$A = (D_c + K_c) - B$$
$$B = 4 \times \left(\frac{1}{D_c} + \frac{1}{K_c}\right)^{-1}$$

In the current case, if $D_c \ll K_c$ is considered, B tends to zero, the expression of D_{eq} will be simplified as:

$$D_{eq} = A \cdot n_{int}$$

Therefore, the model can be rewritten as the following format:

$$\rho_l \Phi \frac{\partial S_l}{\partial h} \left(1 - \frac{\rho_v}{\rho_l} \right) \frac{\partial h}{\partial t} = \mathbf{div} \left[n_{int} \cdot A\left(h, t\right) \cdot \nabla h \right]$$

or,

$$\rho_l \ C_{eq} \ \frac{\partial h}{\partial t} = \mathbf{div} \left[n_{int} \cdot A(h, t) \cdot \nabla h \right]$$
(4.11)

in which,

$$C_{eq} = \Phi \; \frac{\partial S_l}{\partial h} \left(1 - \frac{\rho_v}{\rho_l} \right)$$

If it is close to the real situation that water vapor diffusion is negligible in comparison with the permeation ability of liquid water, it can be deduced that with different interpolation values, a uniformed result can be always found by introducing dimensionless time. Because if we apply any interpolation value of n_1 and n_2 in Eq. 4.11, we get:

$$\rho_l \ C_{eq} \ \frac{\partial h}{\partial t} = \operatorname{div} \left[n_1 \cdot A(h, t) \cdot \nabla h \right]$$
(4.12)

$$\rho_l \ C_{eq} \ \frac{\partial h}{\partial t} = \operatorname{div} \left[n_2 \cdot A(h, t) \cdot \nabla h \right]$$
(4.13)

By defining $t^* = n_2/n_1 \cdot t$, Eq. 4.12 can be modified as Eq. 4.14, namely that the two equations have the same form and solution. This analysis is verified by the simulation results of both relative humidity and mass loss. The unified results of relative mass loss and *RH* are shown in Fig. 4.22 and Fig. 4.23, respectively.

$$\rho_l \ C_{eq} \ \frac{\partial h}{\partial t^*} = \mathbf{div} \left[n_2 \cdot A(h, t) \cdot \nabla h \right]$$
(4.14)

From the unified results of relative mass loss versus modified time (Fig. 4.22), the unique evolution and week deviation are observed and the uniformity doesn't rely on the interpolation factors.

It is also suggested that for small n value, the deviation increases and the such deviation will be less if we consider a more dominant $K_c \gg D_c$.

The results from relative humidity Fig. 4.23 presented similar uniform as results of mass loss. However, the local variability is more obvious than the integral concept of mass loss. The evolution of relative humidity is more pronounced over time, which illustrates an increase of equivalent diffusion coefficient for n close to zero.



Figure 4.22: Uniformed mass loss results with different interpolation values



Figure 4.23: Uniformed relative humidity with different interpolation values

4.3.3 The case of two terms in the same level

In the simulation process, we encounter another situation for the two terms in the diffusion coefficient, which is D_c and K_c are of the same order of magnitude (shown in Fig. 4.24). It shows a similar value for D_c and K_c within the range of relative humidity lower than 80 %.

The two contribution terms in diffusion coefficient profile for this case is drawn in Fig.

4.24. The same interpolation method is applied in this case, to obtain the equivalent diffusion coefficient under different contribution ratio of parallel and series (different interpolation values). Fig. 4.25 shows the equivalent diffusion coefficient profile for different interpolation values.



Figure 4.24: Two contributions in diffusion coefficient profile for the similar level case



Figure 4.25: Equivalent diffusion coefficient profile with different interpolation values for the similar level case

It is observed that when D_c and K_c are relatively equal to each other in a large humidity range, D_{eq} will be independent of interpolation value n_{int} . That is to say no matter how much is the proportion for parallel and series way of moisture transfer, the equivalent diffusion coefficient will be the same value as either permeation term K_c , or diffusion term D_c , which is still a function of saturation degree. It is indicated that $D_{eq} \approx 2K_c$, or $D_{eq} \approx 2D_c$.

Comparing Fig. 4.25 with Fig. 4.19, we discover that when the two terms are relative same order of magnitude, whatever is the value of interpolation, the equivalent diffusion coefficient shows consistent tendency for a large range from relative humidity of 45% to 80%. However, when relative humidity is higher than 80%, the equivalent relative humidity begins to separate and a big difference appears for different interpolation values.

Consequently, the simulation results of mass loss and relative humidity behave high consistence for all the iterations, owing to the constant equivalent diffusion coefficient in our focused range of relative humidity. The simulation results of mass loss and relative humidity with different interpolation values are shown in Fig. 4.26 and Fig. 4.27, respectively.

For the relative humidity at a fixed distance to the drying surface, the profile shows different tendency for the two conditions (compare Fig. 4.21 and Fig. 4.27). For the second case, the diffusion is stronger, resulting to a faster drop of relative humidity and stronger ability of moisture distribution inside porous structures.



Figure 4.26: Simulation result of ML with different interpolation values



Figure 4.27: Simulation result of RH with different interpolation values

To summarize briefly, for the establishing of the original drying model, the moisture transfer of vapor and liquid are treated separately and each phase was considered to take the entire domain and no interaction between them. It provides a simplified approach to establish the model but actually under discussion if it is precise to describe the real mechanism of phenomena.

The study of parallel - series patterns is discussed under two cases, depends on the order of magnitude of the two terms for vapor diffusion and liquid permeation. On one hand if diffusion of vapor is negligible in comparison with the permeation of water, all the results of mass loss and relative humidity at different interpolation values can be unified by applying a method of dimensionless time. That is to say, the results of mass loss evolution and humidity evolution versus time could be predictable on any ratio contributions between parallel and series style.

On the other hand, if the two terms are relative same order of magnitude, a relative consistent results of mass loss and relative humidity profile are obtained regardless of different interpolation values. In short, the parallel and series method supplies a possibility to analyze how proportion of contribution of vapor and liquid affect the drying phenomenon.

4.4 Conclusions

This chapter focuses mainly on the assumptions of the moisture transfer model. The model is characterized by a nonlinear diffusion coefficient. The first attempt is to propose a linear coefficient and obtain a simplified analytical solution. An analogy method with heat transfer problem is adopted to figure out the similar physical process of drying phenomenon. The relative humidity versus time and space is therefore obtained by this simplified method and compared with the nonlinear simulation results.

The second aspect discussion on the model is the moisture transfer pattern, meaning how the liquid and vapor phases of water interact with each other and influence the humidity profile and evolution. This specific assumption explains the moisture transport in a porous structure of combined mode of parallel and series, which is more comprehensive and could be closer to the reality than the original model. Two cases of transfer pattern are considered, either the permeation of liquid water is in dominant position or both the permeation of liquid water and diffusion of water vapor are in relatively in the same order of magnitude. For each case, an interpolation factor is implanted to express the diffusion coefficient and the equivalent coefficient is calculated.

Results show that if vapor diffusion is negligible in comparison to liquid permeation, all the results of mass loss and relative humidity at different interpolation values can be unified by applying a method of dimensionless time. Therefore the results of mass loss evolution and humidity evolution versus time can be predicted on any ratio of contributions between parallel and series styles. While if the two terms are relative same order of magnitude, regardless of the value of interpolation, consistent results of mass loss and relative humidity profile are obtained. As a summary, the parallel and series method supplies a potential approach to study the proportion of contribution of vapor and liquid coupling in the moisture transfer process.

However, this approach is used mainly to analyze the model based on our interested humidity range (higher than 30%). Furthermore, it is related also to the interconnections and the pore distribution, which is one of the main characteristic controlling the water displacement.

Chapter 5 Multi-scale study and 3D reconstruction of porous structures

The properties of material are strongly related to its pore network structures. Such structures provide the specific surface involved in the adsorption process and characterize the storing ability and the transient delay (inertia effect). The inner structure, porosity and distribution govern the diffusion of vapor phase and the permeation of liquid phase. Moreover, they control also the hysteresis adsorption and material behavior [Abdel-Jawad and Hansen, 1988, Sanchez and Sobolev, 2010].

In recent years, more and more literature appears on the subject of 3D structure related to the concrete properties, (permeability, diffusivity, *etc.*) [Halamickova et al., 1995, Amiri et al., 2005, Wu et al., 2020].

First of all, we need to have an overview of the scale of pore networks or particle size in concrete materials. On this issue, we present a modified scale ruler from work of [Sanchez and Sobolev, 2010], as shown in Fig. 5.1. It is suggested that the concrete-related particle size and specific surface area could cover a large scale range from few nanometers to tens of millimeters.

In the field of nanotechnology in concrete, another interesting overview published by Blunt [Blunt et al., 2013] about the permeability in non-saturated porous material, focusing on contaminant transport and carbon dioxide storage. A reconstructed 3D pore networks is presented in Fig. 5.2.



Figure 5.1: Particle size and specific surface area related to concrete materials, modified from [Sanchez and Sobolev, 2010]

The influence of the micro-structure of cementitious materials on their gas permeability, was demonstrated. Such gas permeability is correlated to the total porosity for the cement pastes but no strong correlation can be found for different mortars due to the effect of the aggregate volume and size on the transport properties in the cement paste matrix [Care and Derkx, 2011]. A new test method was developed by Boumaaza [Boumaaza et al., 2018] to determine the gaseous diffusion coefficient through hardened cement pastes conditioned at different relative humidity.

In addition, modernization on network genesis was explored such as work of Ioannidou [Ioannidou et al., 2016], using simulations that combine actions between the nanoscale of C–S–H bricks and their effective interactions integrated in a statistical physics approach for nano-particles aggregating.

Secondly, after knowing the theory and concept, we need practical methods and



Figure 5.2: Pore networks extracted from the 3D images [Blunt et al., 2013]

devices to perform the test or measurement. The popular techniques adopted by researchers to study on pore structures concrete include Mercury Intrusion Porosimetry (MIP), Computed micro-Tomography (micro-CT), Back-Scattered electron (BSE), Helium Iron Microscopy (HIM), Scanning Electron Microscopy coupled with Focused Ion Beam (SEM-FIB), *etc.* [Sanchez and Sobolev, 2010]. Researchers also proposed a promising method by using NMR to study the effects of drying on the water content and the pore size distribution [Faure et al., 2012]. Here we refer to a FIB-SEM result from Song [Song et al., 2019], with a resolution of 10nm/pixel, as shown in Fig. 5.3.

Consequently, in this chapter we will have an investigation of the pore networks on the same concrete material that is used in the moisture transfer experiment. The objective is to obtain the pore size distribution covering a relative large range (tens of nanometers to few millimeters), and to reconstruct the pore networks in 3D, which allows to have a direct visibility of the pore structures of concrete. Furthermore, the second step after we obtain the pore network distribution, is to deduce the properties of the concrete from the micro scale, in order to understand the transport phenomenon in a different aspect, which means to establish an interlink between the micro-structure and the mocro-scale moisture transfer phenomenon. There are three parts included in



Figure 5.3: Process of FIB-SEM imaging: (a) aimed surface in 2D SEM; (b) cropped cross section of cement paste [Song et al., 2019]

this chapter to study the pore structure networks, they are MIP, X-ray tomography and FIB-SEM method:

The MIP method is traditional used to quantify the characteristic of porous materials, such as density, pore volume, pore size distribution, and other porosity-related characteristics [Ma, 2014, Abell et al., 1999, Song et al., 2019]. Despite the pre-treatment of the samples that could change part of the structure, it is an effective approach to have access to smaller pore size (about 6 nm) corresponding to the imposed pressure. The preparation of the samples and experiment process will be introduced and three cube samples $(10 \text{ mm})^3$ are tested. The pore size distribution is obtained and analyzed. As a comparison method, the advantages and disadvantages of this method will be discussed as well.

The computational X-ray tomography method is "non-destructive" and real-time test, it can be performed in the normal indoor ambient [Wang and Dai, 2017, du Plessis and Boshoff, 2019, Bennai et al., 2018]. Materials science is increasingly based on the use of X-ray micro-tomography, since there are strong relationships between macroscopic and microscopic properties [Maire et al., 2001, Landis and Keane, 2010].

The tomography images allow reconstructing three-dimensional visualized images in the oriented object with a resolution of 10.6 $\mu m/pixel$ in this test. Carried out in three cube samples $(10mm)^3$, we obtain the raw data of the tomography images. After a series of image post-processing, the pore bubbles is extracted and reconstructed in 3D visualization. The pore size distribution in the ranged from tens of micrometers to more one millimeter. The calculation algorithm and the post-processing of the images is also presented in this section.

The goal of FIB-SEM test is to investigate concrete inner structure in smaller scale and higher resolution. The resolution of FIB-SEM images in this test reaches a scale as small as 20 nm/pixel. The target domain (area of interest) in this test is $(15 \ \mu m)^3$. We obtain a series of electron image with a resolution of $1536 * 1024 \ pixel^2$. Despite the high resolution of the images, there are also some shortcomings (like charging problem or curtain effect) of this method on concrete materials. The same approach is adopted to obtain the 3D visualization of reconstructed pore structure.



Figure 5.4: A summary map illustrating the multi-scale methods and the corresponding scales

As a summary, a large range of the pore size (from 20nm to 1.1mm) is covered and investigated by the multiple approaches. The 3D view of bubbles in concrete, as well as their size distribution are obtained. A reconstruct of 3D view of pore networks is extracted, with the spatial resolution of 20 nm/pixel. To have a global view of all these testing method and their covering ranges, we draw a figure to summarize all the multi-scale approach and the corresponding scales in the present work, as presented in Fig. 5.4.

5.1 Mercury Intrusion Porosimetry

5.1.1 Introduction and principal of MIP

The porosimetry is generally used to measure the characteristic of porous material, such as density, pore volume, pore size distribution, and other characteristics which are related to porosity. The principle of the method is based on the penetration of liquid into small cylindrical pores. The pores diameters are calculated from the pressure value taking into account the surface tension and the wetting angle of the liquid.

Due to the character of mercury that it doesn't wet most substances and it doesn't intrude spontaneously pores by capillary action, the fluent must be forced into the pores by applying external pressure. The required equilibrium pressure is inversely proportional to the size of the pores, namely, only slight pressure being required to penetrate mercury into large macros pores, whereas much greater pressures are required to force mercury into small pores. Schematic of mercury in equilibrium entering an opening under increasing forces is given in Fig. 5.5 [Corporation, 1996].



Figure 5.5: Schematic of mercury in equilibrium entering an opening under increasing forces [Corporation, 1996]

Mercury porosimetry analysis is the progressive intrusion of mercury into a porous structure under stringently controlled pressures. From the pressure versus intrusion data, the instrument generates volume and size distributions based on Washburn equation (Eq. 5.1) [Washburn, 1921]. Clearly, the more accurate the pressure measurements, the more accurate the resulting pore size data. Therefore, at any pressure, the pores into which mercury has intruded have diameters greater than d(m):

$$d = -4 \ \gamma \ \frac{\cos \theta}{p} \tag{5.1}$$

where d(m) is the pore diameter that is reached at the corresponding pressure; $\gamma(N/m)$ is surface tension for mercury at specific temperature; and p (Pa) is the imposed pressure. By measuring the volume of mercury that intrudes into the sample material at each intrusion pressure, the volume of pores in the corresponding size class will be known.

The total pressure range for the present device is: 3 kPa-200 MPa. As is mentioned previously, the pressure is intruded by two parts successively. The low-pressure part, which is imposed by gas, so the pressure range is from 3 kPa - 100 kPa, according to Eq. 5.1, the corresponding diameters are from 420 $\mu m - 1 \mu m$ (corresponding to from low pressure to high pressure); whereas the high - pressure part is intruded by oil, the pressure range is from 101 kPa - 200 MPa, and the corresponding diameters are from $1 \mu m - 6 nm$ (from low pressure to high pressure to high pressure to high pressure).

The sample to be tested has to be dried, degassed, and precisely weighted. It is placed into a special container, the penetrometer. The column is filled up from its bottom orifice with mercury by a vacuum pump. Then the pressure is increased, first using a low pressure pump, later using the high pressure one. Part of the mercury penetrates into the pores of the sample. This mercury volume change is measured precisely by capacitance change (between the mercury column and the metal surrounding), resistance or radiation intensity. The method provides data about pore size and distribution, bulk density and apparent density of the sample.

There are other limitations when the connectives between all the porosity is not inter-level junctions, so the intrusion in some isolated sites or intermediate bubbles will be counted as the smaller capillary bringing the mercury. So it could be necessary to get the higher pores sizes and if possible the interconnection in order to adjust the identified distribution, *i.e.* the distribution is deduced mainly on the intrusion versus pressure.

5.1.2 Specimen preparation for MIP

All of the specimen are cut from the concrete specimen of drying group, the position is taken randomly. All of them are dried in a climate chamber of 60 $^{\circ}$ C for 24 hours, to make

sure that the inner pores are mostly dry. Otherwise, during the vacuum process of the test, the water vapor can destroy the device. The size of the specimen is $10*10*10mm^3$, and all the specimens are placed in a sealed box with pre-dried silica on the bottom, in order to avoid any absorb of moisture, which is shown in Fig. 5.6.

However, the potential disadvantage of this procedure is that the drying process could induce minor changes in the pore structures, such as micro-cracks appears, or global shrinkage of the specimen, which modifies the pore structures and therefore affects the transfer properties of concrete [Bažant, P. et al., 1987, Benboudjema et al., 2005].



Figure 5.6: The prepared samples in MIP test

5.1.3 Penetrometer and devices

The device used in this test is Micromeritics AutoPore IV, Mercury Porosimeter. The test was performed in MSSMat laborary of CentraleSupélec. It is composed of two pressure-increasing units, the computer part using software of AutoPore IV 9500 V1.05. The penetrometer is specifically for small solid bulk, with a chamber volume of 0.336 ml. The illustration of penetrometer and the sealed sample cup with sample inside is shown in Fig. 5.7.

The penetrometer's type is chosen according to the size of the sample and the estimated porosity. Because at equilibrium state of the final intrusion of mercury, the volume that fill the stem has to be within the range of 10 % - 90 %. The pressure-increasing unit is composed of two different parts: the low pressure part, in which compressed gas is used to increase the pressure and the high pressure part, which is injected high pressure



Figure 5.7: Illustration of penetrometer and the sealed sample cup with sample inside

by oil. The device and the partially enlarged view are shown in Fig. 5.8.



Figure 5.8: Micromeritics AutoPore IV, Mercury Porosimeter (MSSMat, Centrale-Supélec)

5.1.4 Results and discussion for MIP

The three tested samples are named A, B, C. The cumulative intrusion and extrusion curves are plotted in Fig. 5.9. Due to the appearance of aggregates in the samples, and the random cut of the target area, the sample size is too small to represent the global porosity. Therefore, we focus mainly on the pore size distributions of the three samples, instead of specific porosity.



Figure 5.9: Intrusion and extrusion curves in mercury intrusion porosimetry test

It shows obviously the hysteresis in intrusion and extrusion cycles. This phenomenon can be attributed to the so-called "ink-bottle effect" [Moro, 2002, Espinosa and Franke, 2006]. There are various mechanisms proposed by literature to explain the hysteresis, one of the commonly accepted is that the hysteresis is due to the difference contact angle during intrusion and extrusion process between mercury and the solid surface [Porcheron et al., 2007, Collet et al., 2008].

It appears also the interrupt of continuous for extrusion curve. This is because the low-pressure part of mercury intrusion is charged by gas, when the extrusion process begins, it is impossible to decrease the pressure by extract gas once the mercury is intruded. It is noted that the peak intrusion volume shows diversity for these three samples, due to the fact that the specific porosity for each sample is not the same.

Confined to the penetrometer size (Fig. 5.7), the size of our samples is considered as within the REV (illustrated in Fig. 1.4 of Chapter 1). Therefore, the porosity we

Test parameters	А	В	\mathbf{C}	Average value
Porosity (%)	17.11	11.79	8.17	12.36
Bulk Density (g/mL)	2.03	2.24	2.44	2.24
Apparent Density (g/mL)	2.45	2.54	2.65	2.55
Stem Vol. used $(\%)$	47	38	21	35.33
BET surface area (m^2/g)	230	230	230	230
Tot. pore area (m^2/g)	6.17	4.31	4.07	4.85
Tortuosity	33.75	11.64	8.29	17.89

Table 5.1: A summary of the MIP results

obtained in this test can not be taken as a global reference, whereas it is a specific value just for these samples. These samples contain different proportion of aggregate, and only the remaining cement paste contribute to the result of MIP test.

As the aggregates do not significantly contribute to the access of the pore structure, we normalize the cumulative intrusion data. By such approach we capture the intrinsic behavior of the cement mortar. The result is shown in Fig. 5.10, which confirm the unique behavior during the intrusion process. Some minor difference remain, which could be the consequence of errors or contribution of the interface transitional zone (ITZ). The last assumption seem be confirmed by the significant difference on the extrusion curves.



Figure 5.10: Normalized cumulative intrusion curve in MIP

The summary of the results is presented in Table 5.1.

Distribution of pore size for the three samples is obtained in Fig. 5.11, and a local zoom-in figure around the measured critical diameter is also presented Fig. 5.12.



Figure 5.11: Pore size distribution of the three samples



Figure 5.12: A zoom in area of Fig. 5.11

The parameters deduced from MIP results indicate pore structure, and they can be applied based on the statistical or physical meaning. The critical pore diameter can be related to an important macroscopic parameter - permeability of the material. According to Katz–Thompson equation, the relationship is expressed by Eq. 5.2 [Katz
and Thompson, 1986, Katz and Thompson, 1987].

$$\kappa = c \cdot \frac{\sigma}{\sigma_0} \cdot d_c^2 \tag{5.2}$$

where d_c is the critical pore diameter obtained from MIP results, c is an analytical constant depending on pore structure geometry and it equals to 1/226, $\frac{\sigma}{\sigma_0}$ is the reciprocal formation factor and it denotes the pore network connectivity. Indicated from pore size distribution (PSD) results Fig. 5.12, the critical pore diameter is between 0.05 μm to 0.1 μm , the calculated κ will be between 10^{-21} (m^2) to 10^{-17} (m^2), which is coherent with a previous study [Ma, 2014].

However, it is worth noting that due to the "ink-bottle" effect, the pores with smaller size is probably overestimated, which leads to the prediction of permeability lower than the real structure. The previous discussion on the permeability of the model is based on the non-linear characters, we consider that the permeability consists of two mechanisms and the value is related to the local relative humidity value.

5.2 X-ray Tomography test

5.2.1 Introduction of X-ray tomography

X-ray micro-tomography is a non-destructive experimental tool, which allows access to the three-dimensional reconstruction of its microstructure. The spatial resolution of this technique can reach the sub-micrometer [Wang and Dai, 2017, du Plessis and Boshoff, 2019].

The experimental test is carried out in LMT- Cachan, and equipment is shown in Fig. 5.13.

The principle of this technique is shown in Fig. 5.14, and it is based on the Beer-Lambert equation explained by Eq. 5.3 [Light et al., 1994]. The emits source X-rays pass through the sample and reach the detector. For each scan, the sample makes a 360° turn around its axis, taking several images from different angles, and obtaining a digital image.

$$I = I_0 \, exp\left[-\int_l \mu(x)dx\right] \tag{5.3}$$



Figure 5.13: X-ray tomography equipment X 50 (LMT, ENS Paris-Saclay)



Figure 5.14: Working principle of X-ray tomography [Light et al., 1994]

- I_0 is the unattenuated intensity monochrome X-rays ($J \cdot cm^{-2} \cdot s^{-1}$)
- $\mu(x)$ is the attenuation coefficient (cm^{-1})
- I is the transmitted intensity of monochromatic X-rays ($J \cdot cm^{-2} \cdot s^{-1}$)
- -l is the straight line joining the source and detector (cm)

5.2.2 Samples preparation for tomography test

The selection of the elementary representative elementary volume is very critical. The purpose of working at the microscopic scale is to have access to local information and consequently to have a relatively high resolution. Since the resolution is inversely proportional to size of the target samples, one should select the smallest volume to treat for better resolution. On the other hand, the selected volume should represent the physical and morphological parameters at the macroscopic level. To compromise, we determined the test sample size of $10 * 10 * 10 mm^3$.

Three samples (named B2, D2, D4) are tested, the photo of these sample is shown in Fig. 5.15.



Figure 5.15: The tested sample in X-ray tomography

5.2.3 Post-processing and 3D reconstruction of tomography results

The global view generated automatically of the specimen is shown in Fig. 5.16.



Figure 5.16: The global view of tested sample in X-ray tomography

This concrete block is composed of a series of raw images that are obtained in the X-ray tomography test. We will import and treat the image series with the royalty-free image analysis software **ImageJ**. It is an image processing software with a library that is enriched by users. The principal algorithm of estimating particle spacing with its neighboring particles can refer to Appendix C.

We use it in order to identify and analyze the different phases (aggregates, air bubbles, cracks) constituting the concrete. In this part we will focus on the porosity made up of air bubbles. This principle presentation will use *raw* format file from the micro tomograph test. For the description of the principle, we will use 200 images with size of $200 \times 200 \ pixel^2$, to construct a cube. The physical size corresponding to each pixel (3D Voxel) is $10.6\mu m$.

The treatment to identify the different bubbles and their positions and sizes is summarized below. It will consist of a sequence of operations to identify the boundaries of the bubbles. The main objectives of these operations that we will be applied thereafter are as follows (with illustration of Fig. 5.17, and Fig. 5.18):

- Improvement of image sharpness by filtering to reduce photon noise (number of incident photons with statistical variations), and the variability resulting from the electrons generated by the thermal effect even in the absence of a black noise signal and the recording noise resulting from the detector's electronics during signal transformation.
- Improvement of image brightness and contrast based on the histogram of pixel intensities. Adjustment of image brightness and contrast is achieved by vertically translating or rotating the tonal curve, respectively (corresponding to the first and second column of Fig. 5.17).
- Sharpen contours (Sharpen) improves the contrast between a pixel and its neighborhood.
- Image threshold that consists of transforming the 8 (or 16) bit coded image into a binary image (two B & W grey levels). The choice of the threshold level resides in the optimum one chosen in order to make white (black) the levels of grey lower (higher) than this threshold (corresponding to the third column of Fig. 5.17).



Figure 5.17: Post-processing steps to extract spherical shape pores in X-ray tomography results

Detect edges (Find edges, uses the Sobel filter) by calculating the local derivative of the image from the gradient in the vertical and horizontal directions (Fig. 5.18).
Before deriving the image, it is sometimes useful to "plug" the holes, using the Fill Holes function.

An example of a more complete result is shown below in Fig. 5.19 for a cubic sample of dimension $(10 \ mm)^3$ and a resolution of 10.6 $\mu m/pixel$. This result gives the 3D representation of the different bubbles identified and the area of the coarse aggregate in the lower left corner is visible. The distribution of bubble sizes is given in frequency as a function of size. The determination of the porosity is available because it is the sum of the elementary volumes given by the product of the number of bubbles for each size. The given distribution covers bubble diameters of 22 μm to 1.1 mm.

The summary of the statistic parameters in the process is summarized in Table 5.2.



Figure 5.18: Post-processing steps: detect, find edges, and skeletonize analysis along with generate 3D structure



Figure 5.19: Reconstructed 3D view of bubbles in X-ray tomography results

And the histogram of bubbles volume distribution in three samples is obtained and presented in Fig. 5.20.

Assume that the bubbles and pores are in the shape of ball spherical, according to the transform of volume and diameter of spherical $V = 4/3 \pi (d/2)^3$ and resolution of images, the histogram of diameters of bubbles therefore can be obtained (Table. 5.3):

Confined to the resolution, the smallest size that could be withdrawn is $10.6\mu m$, pore

Statistic parameters	D2	D4	B2
min Vol. $(pixel^3)$	10	10	10
max Vol. $(pixel^3)$	172996	655836	318203
No. Bubles	23423	21416	18528
Samp. Size(pixel)	800*800*780	810*810*810	760*760*760
Tot. Vol. $(pixel^3)$	499200000	531441000	438976000
Bub.Vol. $(pixel^3)$	9631153	10235394	9958753
Bub.Ratio(%)	1.92931751	1.92596996	2.26863268

Table 5.2: A summary of the statistic parameters in post-processing

Bubble volume distribution



Figure 5.20: Histogram of bubbles volume distribution in three samples

Table 5.3: Statistic counting of bubble diameters in X-ray tomography results

Diameter(μm)	Frequency D2	Frequency D4	Frequency B2
0-61	13895	12966	10401
100 - 104	6485	5794	5414
104 - 132	1457	1300	1229
132 - 225	1324	1128	1228
225 - 283	151	123	156
283 - 357	61	56	54
357 - 485	39	34	27
485-610	10	8	11
610-770	1	3	4
770 - 1145	0	4	4
and more	0	0	0

size that is smaller is unable to be distinguished.

The 3D bubbles distributed with a size of $(760 \ pixel)^3$ in the sample is presented in Fig. 5.21 and smaller scale $(250 \ pixel)^3$ in Fig. 5.22, respectively.



Figure 5.21: 3D bubbles distributed in the sample $(760 \ pixel)^3$



Figure 5.22: 3D bubbles distributed in the sample $(250 \ pixel)^3$

5.3 FIB-SEM test

5.3.1 Introduction of FIB-SEM

FIB systems was produced commercially approximately twenty years ago, primarily for large semiconductor manufacturers. This systems operate in a similar fashion as SEM. FIB systems use a finely focused ions beam (usually gallium) that can be managed at low beam current for imaging or at high beam current for site specific sputtering or milling [Lim et al., 2018, Blunt et al., 2013, Sanchez and Sobolev, 2010].

There is a tilt different between the electron scanning direction and the iron beam direction, which is around 52° to 54°. The schematic diagram is presented in Fig. 5.23



Figure 5.23: Schematic principle of electron and iron beam of FIB-SEM

5.3.2 Equipment and sample preparation of FIB-SEM

The FIB-SEM test was performed Laboratory MMSMaT of CentraleSupélec, the equipment type is HELIOS NANOLAB 660, which is shown in Fig. 5.24.

The concrete samples used in the FIB-SEM test is the same material as all the other tests, except the size is much smaller (5mm * 5mm * 1mm). It is fixed on a support system before the test starts, which is shown in Fig. 5.25.

Some pretreatment is need for the samples, to make it electrically conductive. The surface of the samples is painted by gold metal, with a thickness of few nanometers. As the target area is $(15\mu m)^3$, this minor thickness is considered negligible to the scanning results of SEM. In addition, at the beginning of the beam cutting, a carbon protection layer is sprayed as well, in order to protect the surface structure from destroying when cutting by ion beam, which is different from the pre-treatment of gold painting to enhance the electric conduction.

The technical parameters during the FIB-SEM test are:



Figure 5.24: Equipment of FIB-SEM



Figure 5.25: Concrete samples in FIB-SEM test

- Target area (area of interest) : $(15 \ \mu m)^3$
- Electron image resolutions : 1536 * 1024 $pixel^2$
- Beam current in target area: 0.79nA
- Beam current in surrounding area: 65 nA (82 times stronger than the beam current

in target area, to save the time of beam cutting, but the disadvantage is that irregular surface is created and micro structures are mostly destroyed.)

Removed area: depth of 15 μm , it is used to create channels on both sides of the target area. when the ion beam is launched to cut, there will be enough space to contain the removed materials from target area, as shown in Fig. 5.26 and Fig. 5.27.



Figure 5.26: Ion beam image with magnification of 1200

5.3.3 Results and 3D reconstruction of FIB-SEM results

The electron image explanations with magnification of 1502 is presented in Fig. 5.27. The green square area is the target area that is to be investigated. The upper part marked in yellow square is the carbon protection layer, and the removed area on both sides of target region are shown in two blue squares.

By adopting the same post-processing as the results in X-ray tomography, we extract the pore networks and get a series of electron images reconstructed. Some chosen images from the 575 series are shown in Fig. 5.28.

We extract the pore networks in FIB-SEM image series, and the 3D reconstruction of the pores are obtained, shown in Fig. 5.29.

This work is still on process in order to complete the previous results, and to complete the multi-scale representation. Such continuum representation coupled with our



Figure 5.27: Explanation of the electron image with magnification of 1502



Figure 5.28: A series of FIB-SEM figures on the scale of 11.5 μm , with resolution of 20 nm/pixel (575 is the total slides number of the image series).

ongoing direct numerical simulation will allow us to get access to the equivalent transfer properties. Some difficulties appears and we will have further description later.

5.4 Conclusions

In this chapter, different approaches are adopted to investigate the inner structure properties of concrete material, including intrusion-extrusion characteristic curve, pore size distribution, and the 3D structure visualization at different scales. The measurements are carried out using three technical methods: the mercury intrusion porosimetry method (MIP), computational X-ray tomography, and the focused ion beam-scanning electron microscope (FIB-SEM).



Figure 5.29: The 3D reconstruction FEB-SEM view for a $(11.5 \ \mu m)^3$ cube with spatial resolution of $(20 \ nm)^3/voxel$

Despite the limitation on samples size, we discovered the unity of the pore networks' characteristics (*e.g.* intrusion-extrusion feature, pore size distribution, presence of air bubbles). The scale of pore structure we obtained in these tests covers large size range from tens of nanometers to few millimeters, which allows us to have a more global inspect of the concrete inner structures. Furthermore, we extract and reconstructed the pore networks to obtain the 3D visualization, which is prospective for the further research on the interlink of material properties with its structures at microscopic scale.

To summarize, in this multi-scale tests, we are able to complete the inner structure porosity by combining the different techniques, especially micro-tomography allowing to access to trapped air bubble and its distribution.

Such distribution and explicit 3D view complete the implicit pore distribution from the results of MIP. It completes the MIP results on the right side of increasing pore sizes. The left side of the size axis was completed by the FIB-SEM techniques and we were able to visualize the local 3D structure on a scale from 20 nm to 150 nm. This local visualization is informative and need more exploration due to the continuous heterogeneity of our materials.

The obtained final structure provide the information of the size, distribution porosity

and access also to the specific surface area. Such properties are key features for sorption phenomena, permeability and diffusivity in the unsaturated situation. The previous parameters versus humidity $(S_l(h), K_c(h), D_c(h))$ are the important functions allowing the simulation/prediction of the local humidity or water content within the material and function of time.

General conclusions & Perspectives

In this thesis work, we focus on the moisture transfer mechanism in concrete, by combination of experimental and numerical approaches. From the perspective of the moisture transfer model and the multi-scale structure of the concrete, we performed the test of drying, imbibition, and drying-imbibition cycling in different geometries of concrete for over 200 days (including RH tests), and obtained the global mass variation and local inner humidity data.

Based on the present model and the experimental results obtained, the simulation results of mass loss and relative humidity is calculated in CAST3M, and an identification produce of parameters in the model is performed in an optimization program coupled with MATLAB. A numerical-experiment-identification coupling method is proposed to predict drying phenomenon, and the results provide a practical approach in following the moisture transfer process of concrete.

A second part related to the pore structure-related properties is a multi- scale approach to investigate the inner structure of concrete material. Through three techniques, we get the results that cover a large range of the pore size, and obtain the 3D visualization of the inner structures of the concrete material.

To be more precise, in Chapter 1, the background of cement-based material concrete is introduced, and one of the significant challenge in its durability - structure deterioration or pathology - is presented and its close relationship with moisture transfer in concrete is also illustrated. Considering cement-based material as porous media, the mechanism of moisture transfer in the porous media is introduced as well.

In Chapter 2, experiments of moisture transfer in concrete are performed in a lab-

oratory environment. The concrete material is named B11. Concrete specimen with different geometries are separated into three groups, subjected correspondingly to the test of desorption of water (drying), adsorption of water (imbibition), and eventually the drying-imbibition cycling. The global mass transfer (mass loss) and local hydrate state (relative humidity) are tracked and recorded regularly. In spite of the difficulties in tracking inner humidity in concrete, we obtained some interesting results as well.

Chapter 3 mainly focused on the moisture-transfer model and the parameters optimization. A non-linear diffusion model concerning two phenomena of liquid water permeation and water vapor diffusion is used to predict the moisture state of the porous cementitious material. The identification procedure of parameters in the model is performed based on an in-house identification tool coupling MATLAB with CAST3M. Calculation on optimization of parameters for different time duration windows and available different sensor positions is analyzed to find out the adequate experimental data within the shortest time duration.

In Chapter 4, the hypothesis or assumptions of the moisture transfer model are discussed. The analysis includes the assumptions that are adopted in the model; a simplified analytical solution with the hypothesis of linear coefficient; and the discussion of moisture transfer pattern in the model, meaning how the two phases (liquid and vapor) of water interact and influence the humidity profile and mass loss evolution.

In the last Chapter 5, we investigate the characteristic of concrete materials inner structure, by multiple approaches, including MIP, X-Ray tomography, and FIB-SEM. The pore size distribution covers a range from few micrometers to millimeters. Meanwhile we reconstruct the 3D structure of the bubbles distribution in concrete material.

The main contributions of this work as well as perspectives can be concluded as the following.

Based on the parameters function (admitted forms), we identify numerically the values of the controlling coefficients using reliable database that are obtained experimentally in drying, imbibition and drying-imbibition cycles. The used identification is robust because using the classical ML history from different geometries enriched by several local humidity history.

The use of global (ML) and local (RH) information over time is one of important improvement. The development of accurate local humidity measurement is one of the goal to afford fast response in time and to avoid the sensor to be "blind" when liquid water is formed and in contact with it.

The combination of the experimental and numerical work permits to give prescription and protocol on the position and number of needed humidity probes and the test duration to get identified physical parameters within the fixed tolerance.

The identification process uses the common admitted transfer model combining the parallel fluxes of humidity transfer and water permeation. Based on the interlinked multi-scale structure, we knew that liquid bridges and multiple liquid-gas interfaces settle inside the porous media. Such spatial water contents complexity (especially in Drying-Imbibition cycle) will contradict the parallel flux approach.

We include in the model a parallel-serial approach and we reuse the identification process to analyze the evolution of identified physical properties. Several regime and behavior were identified based on the relative importance of the flux contribution of the diffusivity and permeation.

Moreover to the complexity, we explored the condition of simplification where the linear coefficient that can answer on the global evolution of humidity/water contents evolution over time. The linearized approach (constant diffusivity and permeation) allows to quantify the deviation of the results from the obtained one based on the complex model. The results underline the physical contributions of the fluxes on the material bulk (moderate RH values) and in the direct vicinity of the equivalent liquid-gas interface (high RH values). Interesting features were demonstrated and more complex expecially for the case of drying-imbibition cycles.

In the multi-scale tests, we complete the inner structure porosity by combining the different techniques, especially micro-tomography that allows to access to trapped air bubble and their distribution. Such distribution and explicit 3D view complete the implicit pore distribution from the results of MIP on the right side of increasing pore sizes, and the left side of the size axis was completed by the FIB-SEM techniques. We visualize the local 3D structure at a micro scale from 20 nm - 150 nm. This local visualization is informative and need more exploration due to the continuous heterogeneity of our materials.

The obtained final structure provides information of the size, distribution porosity and access also to the specific surface area. Such properties are key features for sorption phenomena, permeability and diffusivity in the unsaturated situation. The key parameters in the moisture transfer model are all function of humidity $(S_l(h), K_c(h))$ and $D_c(h)$, and they are the important parameters allowing the simulation/prediction of the local humidity/water content within the material and function of time.

As a perspective of the future study, some propositions and suggestions can be given based on the obtained results.

As the preliminary results exhibit strong anisotropy due to the limitation of analyzed samples, we propose to increase the number of samples in order to identify an average behavior with a deviation of the properties. Based on that, a simulated equivalent structure will be more adequate. The interlink of the micro-capillaries, micro-bubbles and bubble are key factors for predicting.

A correlation between the identified properties (coupling of numerical and experimental) and the obtained local structure is also ongoing. With such structure we will have also the possibility to include the sorption curve in order to quantify the equivalent transfer properties versus humidity level. The second limitation and question are related to the limitation of continuum conservative equation (species, momentum, *etc.*) in regard to the Knudsen number on such scale. Two possible perspective investigations could concern the:

Explicit connection between the multi-scale porous structures and the physical properties based on physical explanation instead of the used available fitting expression;
The model improvement based on the series/parallel fluxes contribution consequence of the material structure (especially when evolving over time): on one hand to predict the water contents distribution, and on the other hand to analyze better the drying-imbibition cycles.

Bibliography

- [Abdel-Jawad and Hansen, 1988] Abdel-Jawad, Y. and Hansen, W. (1988). Pore structure of hydrated cement determined by mercury porosimetry and nitrogen sorption techniques. MRS Proceedings, 137:105.
- [Abell et al., 1999] Abell, A. B., Willis, K. L., and Lange, D. A. (1999). Mercury intrusion porosimetry and image analysis of cement-based materials. *Journal of Colloid* and Interface Science, 211(1):39-44.
- [Aligizaki, 2006] Aligizaki, K. K. (2006). Pore Structure of Cement-Based Materials (Modem Concrete Technology series).
- [Amiri et al., 2005] Amiri, O., AMokhtar, A., and Sarhani, M. (2005). Tri-dimensional modelling of cementitious materials permeability from polymodal pore size distribution obtained by mercury intrusion porosimetry tests. Advances in Cement Research, 17(1):39-45.
- [Andrew, 2018] Andrew, R. M. (2018). Global CO₂ emissions from cement production. Earth System Science Data Discussions, 10:195–217.
- [Baroghel-Bouny, 2007a] Baroghel-Bouny, V. (2007a). Water vapour sorption experiments on hardened cementitious materials. Part I: Essential tool for analysis of hygral behaviour and its relation to pore structure. *Cement and Concrete Research*, 37(3):414–437.
- [Baroghel-Bouny, 2007b] Baroghel-Bouny, V. (2007b). Water vapour sorption experiments on hardened cementitious materials. Part II: Essential tool for assessment of transport properties and for durability prediction. Cement and Concrete Research, 37:438-454.

- [Baroghel-bouny,V., 1994] Baroghel-bouny,V. (1994). Caractérisation microstructurale et hydrique des pâtes de ciment et des bétons ordinaires et à très hautes. PhD thesis, Ecole Nationale des Ponts et Chaussées.
- [Basheer et al., 2001] Basheer, L., Kropp, J., and Cleland, D. J. (2001). Assessment of the durability of concrete from its permeation properties: a review. *Construction and Building Materials*, 15(2):93 – 103.
- [Bažant, P. et al., 1987] Bažant, P., Z., Sener, S., and Kim, J.-K. (1987). Effect of cracking on Drying Permeabiliy and Diffusivity of Concrete P.Zdenek. ACI Materials Journal, 84-M35:351-357.
- [Bazant and Bažant, 2012] Bazant, M. Z. and Bažant, Z. P. (2012). Theory of sorption hysteresis in nanoporous solids: Part II Molecular condensation. Journal of the Mechanics and Physics of Solids, 60(9):1660-1675.
- [Bear, 1972] Bear, J. (1972). Dynamics of fluids in porous media. Number V.2. American Elsevier, New York.
- [Benboudjema et al., 2005] Benboudjema, F., Meftah, F., and Torrenti, J. M. (2005). Interaction between drying, shrinkage, creep and cracking phenomena in concrete. *Engineering Structures*, 27(2):239–250.
- [Bennai et al., 2018] Bennai, F., El Hachem, C., Abahri, K., and Belarbi, R. (2018). Microscopic hydric characterization of hemp concrete by X-ray microtomography and digital volume correlation. *Construction and Building Materials*.
- [Blunt et al., 2013] Blunt, M. J., Bijeljic, B., Dong, H., Gharbi, O., Iglauer, S., Mostaghimi, P., Paluszny, A., and Pentland, C. (2013). Pore-scale imaging and modelling. Advances in Water Resources, 51:197 – 216. 35th Year Anniversary Issue.
- [Boumaaza et al., 2018] Boumaaza, M., Huet, B., Pham, G., Turcry, P., Ait-Mokhtar, A., and Gehlen, C. (2018). A new test method to determine the gaseous oxygen diffusion coefficient of cement pastes as a function of hydration duration, microstructure, and relative humidity. *Materials and Structures*, 51(2).

- [Briffaut et al., 2011] Briffaut, M., Benboudjema, F., Torrenti, J. M., and Nahas, G. (2011). Numerical analysis of the thermal active restrained shrinkage ring test to study the early age behavior of massive concrete structures. *Engineering Structures*, 33(4):1390-1401.
- [Brunauer, 1943] Brunauer, S. (1943). The Adsorption of Gases and Vapors: Physical adsorption. Princeton University Press.
- [Brunauer and Copeland, 1964] Brunauer, S. and Copeland, L. E. (1964). The Chemistry of Concrete. *Scientific American*, 210(4):80–93.
- [Care and Derkx, 2011] Care, S. and Derkx, F. (2011). Determination of relevant parameters influencing gas permeability of mortars. *Construction and Building Materi*als, 25(3):1248–1256.
- [Carette et al., 2016] Carette, J., Benboudjema, F., Nahas, G., and Abahri, K. (2016). Analysis of drying in concrete: effects of boundary conditions and specimen size/ shape. In International RILEM Conference on Materials, Systems and Structures in Civil Engineering, number August, Lyngby, Denmark.
- [Carette et al., 2020] Carette, J., Soleilhet, F., Benboudjema, F., Ma, X., Nahas, G., Abahri, K., Darquennes, A., and Bennacer, R. (2020). Identifying the mechanisms of concrete drying: An experimental-numerical approach. *Construction and Building Materials*, 230:117001.
- [Carlier et al., 2012] Carlier, J., Rougelot, T., and Burlion, N. (2012). Performance evaluation of models describing sorption isotherm in cementitious materials between saturation and oven dryness. *Construction and Building Materials*, 37:58–66.
- [Collet et al., 2008] Collet, F., Bart, M., Serres, L., and Miriel, J. (2008). Porous structure and water vapour sorption of hemp-based materials. *Construction and Building Materials*, 22(6):1271–1280.

[Corporation, 1996] Corporation, M. I. (1996). Mercury intrusion porosimetry theory.

[Crank, 1975] Crank, J. (1975). The Mathematics of Diffusion.

- [Darcy, 1856] Darcy, H. (1856). Les fontaines publiques de la ville de Dijon : exposition et application des principes à suivre et des formules. Les fontaines publiques de la ville de Dijon. Paris: Dalmont.
- [Derluyn et al., 2012] Derluyn, H., Derome, D., Carmeliet, J., Stora, E., and Barbarulo, R. (2012). Hysteretic moisture behavior of concrete: Modeling and analysis. *Cement* and Concrete Research, 42(10):1379–1388.
- [Diment and Watson, 1985] Diment, G. A. and Watson, K. K. (1985). Stability analysis of water movement in unsaturated porous materials: 3. experimental studies. *Water Resources Research*, 21(7):979–984.
- [du Plessis and Boshoff, 2019] du Plessis, A. and Boshoff, W. P. (2019). A review of X-ray computed tomography of concrete and asphalt construction materials. *Con*struction and Building Materials, 199:637–651.
- [Espinosa and Franke, 2006] Espinosa, R. M. and Franke, L. (2006). Inkbottle Pore-Method: Prediction of hygroscopic water content in hardened cement paste at variable climatic conditions. *Cement and Concrete Research*, 36(10):1954–1968.
- [Faure et al., 2012] Faure, P. F., Caré, S., Magat, J., and Chaussadent, T. (2012). Drying effect on cement paste porosity at early age observed by nmr methods. *Construction and Building Materials*, 29:496 - 503.
- [Granja et al., 2014] Granja, J. L., Azenha, M., de Sousa, C., Faria, R., and Barros, J. (2014). Hygrometric assessment of internal relative humidity in concrete: Practical application issues. *Journal of Advanced Concrete Technology*, 12(8):250-265.
- [Greenspan, 1977] Greenspan, L. (1977). Humidity Fixed Points of Binary Saturated Aqueous Solutions. Journal of Research of the National Bureau of Standards - A. Phys ics and Chemistry, 81A(1):89–96.
- [Haeri and Haeri, 2015] Haeri, M. and Haeri, M. (2015). ImageJ Plugin for Analysis of Porous Scaffolds used in Tissue Engineering. *Journal of Open Research Software*, 3:2–5.

- [Halamickova et al., 1995] Halamickova, P., Detwiler, R. J., Bentz, D. P., and Garboczi,
 E. J. (1995). Water permeability and chloride ion diffusion in portland cement mortars: Relationship to sand content and critical pore diameter. *Cement and Concrete Research*, 25(4):790 - 802.
- [Hilaire, 2014] Hilaire, A. (2014). Étude des déformations différées des bétons en compression et en traction, du jeune âge au long terme. PhD thesis, L'école Normale Supérieure de Cachan.
- [Ioannidou et al., 2016] Ioannidou, K., Krakowiak, K. J., Bauchy, M., Hoover, C. G., Masoero, E., Yip, S., Ulm, F.-J., Levitz, P., Pellenq, R. J.-M., and Del Gado, E. (2016). Mesoscale texture of cement hydrates. *Proceedings of the National Academy* of Sciences, 113(8):2029-2034.
- [Issaadi et al., 2017] Issaadi, N., Hamami, A. A., Belarbi, R., and Ait-Mokhtar, A. (2017). Experimental assessment of the spatial variability of porosity, permeability and sorption isotherms in an ordinary building concrete. *Heat and Mass Transfer*, 53(10):3037–3048.
- [IUPAC, 1985] IUPAC (1985). International Union of Pure and Applied Chemistry. Reporting physisorption data for Gas/solid systems with special reference to the determination of surface area and porosity. Technical Report 4.
- [IUPAC, 1994] IUPAC (1994). International Union of Pure and Applied Chemistry. Recommendations for the characterization of porous solids. Technical Report 8.
- [Johannesson and Janz, 2009] Johannesson, B. and Janz, M. (2009). A two-phase moisture transport model accounting for sorption hysteresis in layered porous building constructions. *Building and Environment*, 44(6):1285–1294.
- [Katz and Thompson, 1986] Katz, A. J. and Thompson, A. H. (1986). Quantitative prediction of permeability in porous rock A. *Physical Review B*, 34(11):8179.
- [Katz and Thompson, 1987] Katz, A. J. and Thompson, A. H. (1987). Prediction of rock electrical conductivity from mercury injection measurements. *Journal of Geophysical Research: Solid Earth*, 92(B1):599–607.

- [Kumar Mehta, 2006] Kumar Mehta, P.; Paulo, J. M. M. (2006). Concrete: Microstructure, Properties, and Materials, Third Edition.
- [Landis and Keane, 2010] Landis, E. N. and Keane, D. T. (2010). X-ray microtomography. *Materials Characterization*, 61(12):1305–1316.
- [Li et al., 2018] Li, T., Liu, B., Ma, X., and Bennacer, R. (2018). Nanofluid Al₂O₃-H₂O evaporation: Energy and deposition patterns. *EPJ Applied Physics*, 83(1):10903.
- [Light et al., 1994] Light, L. B., Huebner, J. S., and Vergenz, R. A. (1994). How Does Light Absorption Intensity Depend on Molecular Size? Journal of Chemical Education, 71(2):105.
- [Lim et al., 2018] Lim, S., Lee, H. S., and Kawashima, S. (2018). Pore structure refinement of cement paste incorporating nanosilica: Study with dual beam scanning electron microscopy/focused ion beam (SEM/FIB). *Materials Characterization*, 145(August):323-328.
- [Liu et al., 2011] Liu, X., Schnell, S. K., Simon, J. M., Bedeaux, D., Kjelstrup, S., Bardow, A., and Vlugt, T. J. (2011). Fick diffusion coefficients of liquid mixtures directly obtained from equilibrium molecular dynamics. *Journal of Physical Chemistry* B.
- [Lu and Viljanen, 2011] Lu, X. and Viljanen, M. (2011). Fibrous insulation materials in building engineering applications. In Fangueiro, R., editor, *Fibrous and Composite Materials for Civil Engineering Applications*, Woodhead Publishing Series in Textiles, pages 271 – 305. Woodhead Publishing.
- [Ma, 2014] Ma, H. (2014). Mercury intrusion porosimetry in concrete technology: Tips in measurement, pore structure parameter acquisition and application. *Journal of Porous Materials*, 21(2):207–215.
- [Ma et al., 2018a] Ma, X., Benboudjema, F., and Bennacer, R. (2018a). Thermal and water transfer in cementitious porous medium: Thermal building and durability. MATEC Web of Conferences, 240:0–4.

- [Ma et al., 2018b] Ma, X., Benboudjema, F., Nahas, G., Bennacer, R., and Cachan (2018b). Experimental and numerical study on moisture transport in unsaturated porous medium. In Int. Conf. Mater. Energy 2018.
- [Ma and Bennacer, 2019] Ma, X. and Bennacer, R. (2019). Study of capillarity dynamics: competition between capillary heterogeneous media. In Int. Conf. Mater. Energy 2019.
- [Ma et al., 2020] Ma, X., Carette, J., Benboudjema, F., and Bennacer, R. (2020). Optimization of experiment methodology based on identification of parameters in concrete drying. *Construction and Building Materials*, 256:119421.
- [Ma et al., 2017] Ma, X., Darquennes, A., Benboudjema, F., Nahas, G., and Bennacer, R. (2017). Study of drying and imbibition cycles in concrete : effects of sample shape and boundary condition. In Int. Conf. Mater. Energy 2017.
- [Maire et al., 2001] Maire, E., Buffière, J. Y., Salvo, L., Blandin, J. J., Ludwig, W., and Létang, J. M. (2001). On the Application of X-ray Microtomography in the Field of Materials Science. Advanced Engineering Materials, 3(8):539–546.
- [Millington and Quirk, 1961] Millington, R. J. and Quirk, J. P. (1961). Permeability of porous solids. Trans. Faraday Soc., 57:1200–1207.
- [Moré, 1978] Moré, J. J. (1978). The levenberg-marquardt algorithm: Implementation and theory. In Watson, G. A., editor, *Numerical Analysis*, pages 105–116, Berlin, Heidelberg. Springer Berlin Heidelberg.
- [Moro, 2002] Moro, F. H. B. (2002). Ink-Bottle Effect in Mercury Intrusion Porosimetry of Cement-Based Materials. *Journal of Colloid and Interface Science*, 246:135–149.
- [Mualem, 1976] Mualem, Y. (1976). A new model for predicting the hydraulic conductivity of unsaturated porous media. Water Resources Research, 12(3):513-522.
- [Naono and Hakuman, 1993] Naono, H. and Hakuman, M. (1993). Analysis of Porous Texture by Means of Water Vapor Adsorption Isotherm with Particular Attention to Lower Limit of Hysteresis Loop. Journal of Colloid and Interface Science, 158(1):19– 26.

- [Neggers et al., 2015] Neggers, J., Hoefnagels, J. P. M., Geers, M. G. D., Hild, F., and Roux, S. (2015). Time-resolved integrated digital image correlation. *International Journal for Numerical Methods in Engineering*, 103(3):157–182.
- [Olivier and Peters, 2019] Olivier, J. and Peters, J. (2019). Trends in global CO₂ and total greenhouse gassummary of the 2019 report. Technical Report December 2019.
- [Omar, 2004] Omar, M. (2004). Drmations différées du béton: étude expérimentale et modélisation numérique de linteraction fluage-endommagement. PhD thesis, ECN Nantes.
- [Oxfall et al., 2016] Oxfall, M., Johansson, P., and Hassanzadeh, M. (2016). Longterm hygrothermal performance of nuclear reactor concrete containments - laboratory evaluations of measurement setup, in situ sampling, and moisture flux calculations. *Cement and Concrete Composites*, 65:128–138.
- [Ozbolt et al., 2016] Ozbolt, J., Orsani, F., and Balabani, G. (2016). Modeling influence of hysteretic moisture behavior on distribution of chlorides in concrete. *Cement and Concrete Composites*, 67:73 – 84.
- [Porcheron et al., 2007] Porcheron, F., Thommes, M., Ahmad, R., and Monson, P. A. (2007). Mercury Porosimetry in Mesoporous Glasses: A Comparison of Experiments with Results from a Molecular Model. *Langmuir*, 23(6):3372–3380.
- [Pujol, 2007] Pujol, J. (2007). The solution of nonlinear inverse problems and the Levenberg-Marquardt method. *Geophysics*, 72(4):W1–W16.
- [Sanchez and Sobolev, 2010] Sanchez, F. and Sobolev, K. (2010). Nanotechnology in concrete a review. Construction and Building Materials, 24(11):2060 – 2071.
- [Sleiman et al., 2012] Sleiman, H., Amiri, O., Ait-Mokhtar, A., and Loche, J.-M. (2012). Chloride transport through unsaturated concrete: chloride profile simulations and experimental validation. *Magazine of Concrete Research*, 64(4):351–359.
- [Song et al., 2019] Song, Y., Zhou, J.-w., Bian, Z.-n., and Dai, G.-z. (2019). Pore Structure Characterization of Hardened Cement Paste by Multiple Methods. Advances in Materials Science and Engineering, 2019:3726953.

- [Troeh et al., 1982] Troeh, F. R., Jabro, J. D., and Kirkham, D. (1982). Gaseous diffusion equations for porous materials. *Geoderma*, 27(3):239–253.
- [van Genuchten, 1980] van Genuchten, M. T. (1980). A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. Soil Science Society of America Journal, 44(5):892–898.
- [Wang and Dai, 2017] Wang, Y.-s. and Dai, J.-g. (2017). X-ray computed tomography for pore-related characterization and simulation of cement mortar matrix. NDT and E International, 86:28–35.
- [Washburn, 1921] Washburn, E. W. (1921). The dynamics of capillary flow. *Phys. Rev.*, 17:273–283.
- [Wu et al., 2020] Wu, Y., Tahmasebi, P., Yu, H., Lin, C., Wu, H., and Dong, C. (2020). Pore ? Scale 3D Dynamic Modeling and Characterization of Shale Samples : Considering the Effects of Thermal Maturation. *Journal of Geophysical Research : Solid Earth*, 125:e2019JB018309.
- [Zhang et al., 2015] Zhang, J., Wang, J., and Han, Y. (2015). Simulation of moisture field of concrete with pre-soaked lightweight aggregate addition. *Construction and Building Materials*, 96:599-614.

Appendix

Appendix A: Relationship of salt solution and RH

Humidity chambers or generators are usually expensive and complex. Whereas humidity equilibrium of chemical systems is a relatively inexpensive and simple approach to control humidity. Among the chemical systems, the most used for this purpose include glycerine and water solutions , aqueous sulphuric acid solutions, and single or binary salt solutions. Such solution provides a degree of humidity adjustment that is achieved by changing the concentration. The concentrations of solutions must be measured and controlled carefully. It is because the presence of unexpected humidity sources or sinks in the system and even the initial equilibrium process can alter the solution concentration.

The following table [Greenspan, 1977] provides the corresponding relationship of some salt solution and value of relative humidity.

TABLE 3. Comparison of Relative Humidity Values of Selected Saturated Salt Solutions for Various Compilations

										Relative	e Humidi	ty, %									
Saturated Salt		10°	C				20 °(e					30	°C					40 °C		
	а	q	c	q	a	q	J	q	e	f	а	р	с	р	e	f	g	р	с	р	e
Potassium Hydroxide	12.34			13	9.32			6			7.38			2			6.26			9	
Lithium Chloride	11.29	14		13	11.31	12		12		15	11.28	12		12		-	11.21	11		11	
Potassium Acetate	23.38	21		24	23.11	22		23		20	21.61	22		22							
Magnesium Chloride	33.47	34	34.7	34	33.07	33	33.1	33	33		32.44	33	31.7	33	32		31.60	32	31.3	32	32
Sodium Iodide	41.83			42	39.65			39			36.15			36			32.88			33	
Potassium Carbonate	43.14	47	47.0	47	43.16	44	44.0	44	42		43.17	43	43.0	43							
Magnesium Nitrate	57.36	57		57	54.38	55		55			51.40	52		52			48.42	49		49	
Sodium Bromide					59.14					58											
Cobalt Chloride											61.83		61.9				55.48		56.6	×	
Potassium Iodide	72.11			72	69.90			20			67.89			68							
Sodium Chloride	75.67	26	76.9	76	75.47	76	75.8	26	26		75.09	75	75.1	75	75		74.68	75	74.4	75	75
Ammonium Chloride					79.23				79.2	79.2	77.90				79.5	79.5					
Potassium Bromide	83.75		86.0		81.67		84.0			84	80.27		82.0				79.43		80.0		
Ammonium Sulfate	82.06	82		82	81.34	81		81	81	81.0	80.63	80		80	81.1	81.1	79.91	62		62	81.1
Potassium Chloride	86.77	88	87.4	88	85.11	86	86.3	86	86		83.62	85	84.5	84	84		82.32	82	82.8	82	83
Potassium Nitrate	95.96	95	95.1	95	94.62	93	94.2	93			92.31	91	92.5	91			89.03	88	89.4	88	
Potassium Sulfate	98.18	98	98.2	98	97.59	26	97.1	26	96.5		97.00	96	96.6	96	96.5		96.41	96	96.1	96	96.5
a Values from this work.	10 -		-	-																	
D Values from references 2	4 and 25	which a	are luent	Ical.																	

WHICH b Values from references 24 and 2 c Values from reference 26. d Values from reference 27. e Values from reference 28. f Values from reference 29.

Appendix B: Response of relative humidity sensors in air

A preliminary tests for response of relative humidity sensors in air was carried out before the experiment work.

1. Tests procedure

Four Ahlborn FHA 646R (T + HR) sensors are subjected to 44.4%, 78.3%, 84.3%, 92.8% and 99.4% RH steps in desiccators. The sensors are named 0.50, 0.51, 0.55 and 0.59.

2. Results

For each sensor, the following RH changes are made:

- From 99.4% to 92.8% (figure a)

- From 92.8% to 84.3% (figure b)

- From 84.3% to 78.3% (figure c)

- From 78.3% to 44.4% (figure d)

- From 44.4% to 99.4% (figure e)

In addition, given the sensitivity of the measurement to the temperature of the sensor, a temperature request is made, taking the base of the sensor in hand for 10 seconds while it remains in the desiccator (at constant temperature and RH). This results in an increase in the temperature measured between 0.5 °C and 1 °C (figure f).

We deduce from these tests the following:

- The response time of the sensors subjected to a given RH is less than 30 minutes, whatever the variation in RH imposed.

- For small variations in RH, the response time of the sensors is less than 10 minutes. Changing the sensor temperature when changing the desiccator also contributes to this response time.

- The 0.59 sensor is clearly defective for RH> 93%. In general, its response time is higher.

- The variation in RH measurement between two sensors can be up to around 3% RH.

- For an environment with constant temperature and relative humidity, an increase in the temperature of the sensor by 1 °C implies approximately a decrease in RH measured by 3%. This implies that when measuring in concrete, it must be ensured that the

temperature of the sensor is set at the same temperature as concrete, and not subject to variations in ambient air temperature.



The figures of Relative humidity & Temperature versus time for different applied humidity sudden changes, from 99.4 % to 92.8 % (a) ; from 92.8% to 84.3% (b) ; from 84.3% to 78.3% (c) ; from 78.3% to 44.4% (d) ; from 44.4% to 99.4% (e).

Appendix C: Algorithm of estimating particle spacing with software of ImageJ

In a close packed configuration of particles/fibers having a circular cross section in 2D space there are 6 immediate neighbors surrounding each particle. In randomly packed systems, coordination number depends on the visual perception and can be lower or higher. Estimation of particle spacing of a particle with its neighboring particles is performed as follows [Haeri and Haeri, 2015]:

- The centroid coordinates of each particle (X,Y) is derived from the result table of the built-in Analyse Particles plugin.
- A circle is fit on each particle with the center (X,Y) and radius r.
- The spacing (wall thickness) between a pair of particles (d) is calculated as:

$$r_1$$
 d r_2 r_2

$$d = \sqrt{(Y_2 - Y_1)^2 + (X_2 - X_1)^2} - (r_1 + r_2)$$

- The distances of each particle with all the other particles is stored in an array and sorted.
- Depending on the coordination number of interest, average of the distances is calculated.
- Results are shown in a new result table, which contain the distance of the closest neighbor to each particle, the average wall thickness, and the average distance of the closest neighbors.


ECOLE DOCTORALE N°579 sciences mécaniques et énergétiques, matériaux et géosciences (SMEMaG)

Title : Experimental and numerical study on moisture transfer dynamics in multiscale porous cementitious materials

Keywords : complex porous material; relative humidity; moisture transferring model; parameters optimization; multi-scale structure

Abstract :

Climate change in the last decades is increasingly influenced by humans activities including the emission of greenhouse gases. In the construction field, cement production contributes to about eight percent of the world's carbon dioxide emissions, due to the fact that concrete is the most widely used manufactured material in existence. Therefore, the sustainability of concrete and the durability of their structures have significant concerns of the global energy consumption and worldwide environmental impact.

Research results showed that the structural behavior of concrete is closely related to the variation of water level in concretes and the loss of free water may induce a modification of its elastic properties, strengths, shrinkage, or creep deformations. Thus, the knowledge of the hydric state of concrete is of utmost importance regarding the mechanical behavior and durability potential of concrete structures. From a microstructure perspective, the properties of moisture transfer is a manifestation of the internal pore structures. Therefore, it is also important to acquire the knowledge of the pore networks and the pore size distribution over a large range of the material.

In this thesis work, we investigate the moisturetransferring mechanisms in concrete with a combination approach of experiment and simulation. From the perspective of the drying model and the multi-scale structure of the concrete, we performed the experiments of drying, imbibition, and dryingimbibition cycles under controlled ambient condition for different geometries of concrete. The experimental work lasts over 200 days, obtaining the global mass variation and local inner humidity data. The moisture-transferring model contains two major mechanisms: liquid water permeation and water vapor diffusion. Based on the present model and the experimental results obtained, the simulation results of mass loss and relative humidity are calculated in CAST3M. In addition, an identification produce of parameters in the model is performed in an optimization program embedded in Matlab. A numerical-experimentidentification coupling method is thus proposed to simulate drying phenomenon, and the results provide a practical approach in following the moisture transfer process of concrete.

Following the parameters optimization, the hypothesis and assumptions in moisturetransferring model are discussed as well. The analysis includes the assumptions that are proposed in the model; a simplified analytic solution with the hypothesis of linear coefficient; and the moisture transferring pattern in the model, explaining if the two phases (liquid and vapor) of water interact in a parallel, series or combination style, how it influences the humidity profile and mass evolution.

The last part of investigation of the concrete is a multiple approaches to study the inner structure of concrete material, including mercury intrusion porosimetry method (MIP), computational X-Ray tomography, and focused ion beam-scanning electron microscope (FIB-SEM). By adopting these three techniques, we obtain the pore size distribution that covers a large range from tens of nanometers to few millimeters. Furthermore, the 3D visualization of the inner structures of the concrete material is reconstructed as well.



ECOLE DOCTORALE N°579 sciences mécaniques et énergétiques, matériaux et géosciences (SMEMAG)

Tittre : Expérience et étude numérique sur la dynamique de transfert d'humidité dans les matériaux cimentaires poreux à plusieurs échelles

Mots clés : matériau poreux complexe; humidité relative ; modèle de transfert d'humidité; optimisation des paramètres; structure multi-échelles

Résumé :

Le changement climatique au cours des dernières décennies est fortement influencé par les activités humaines, y compris l'émission de gaz à effet de serre. Dans le domaine de la construction, la production de ciment contribue à environ huit pour cent des émissions mondiales de dioxyde de carbone, du fait que le béton est le matériau manufacturé le plus utilisé qui existe. Par conséquent, en plus de la sécurité, la durabilité du béton et la durabilité de leurs structures représentent des préoccupations importantes concernant la consommation d'énergie et l'impact environnemental mondial.

Les résultats de la recherche ont montré que le comportement structurel du béton est étroitement lié à la variation du niveau d'eau en son sein et la perte d'eau libre peut induire une modification de ses propriétés chimiques, élastiques, résistances, retrait ou déformations de fluage. Ainsi, la connaissance de l'état hydrique du béton est de la plus haute importance en ce qui concerne l'évolution du comportement mécanique et le potentiel de durabilité des structures en béton. Du point de vue de la microstructure, la propriété du transfert d'humidité est une liée aux structures internes des pores. Par conséquent, il est également important d'acquérir la connaissance des réseaux de pores et de la distribution de leurs taille sur une large gamme de matériau.

Dans ce travail de thèse, nous nous concentrons sur les mécanismes de transfert d'humidité dans le béton, par la combinaison de l'approche expérimentale et numérique. Du point de vue du modèle de séchage et de la structure multi-échelle du béton, nous avons effectué des tests de séchage, d'imbibition et de cycles séchage-imbibition dans différentes géométries de béton pendant plus de 200 jours. Nous avons ainsi obtenu base de donnée fiable sur l'évolution de masse globale des éprouvettes et l'humidité intérieure locale en différents points.

Le modèle de transfert d'humidité contient deux mécanismes principaux: la perméation de l'eau liquide et la diffusion de la vapeur d'eau. Sur la base des résultats expérimentaux obtenus et les résultats de simulation (présent modèle) de la perte de masse et de l'humidité calculés par CAST3M, une d'identification des paramètres de ce modèle est effectué par un programme d'optimisation couplé à Matlab. Cette méthode de couplage numérique-expérience-identification est adoptée pour simuler de façon fiable le phénomène de séchage, et les résultats fournissent une approche pratique pour suivre le processus de transfert d'humidité du béton.

Après l'optimisation des paramètres, les hypothèses du modèle de transfert d'humidité sont également discutées. L'analyse comprend les hypothèses qui sont proposées dans le modèle ; Une solution analytique simplifiée avec l'hypothèse de coefficient linéaire ; Et le schéma de transfert d'humidité dans le modèle, disant si les deux phases (liquide et vapeur) de l'eau interagissent dans un style parallèle, en série ou en combinaison et comment cela influence le profil d'humidité et l'évolution de la masse.

La dernière partie du travail consiste en plusieurs approches pour étudier la structure interne du matériau en béton, combinant la méthode de porosimétrie par intrusion de mercure (MIP), la tomographie par rayons X et le microscope électronique à balayage à faisceau ionique focalisé (FIB-SEM). En adoptant ces trois techniques, nous obtenons la distribution de la taille des pores qui couvre une large gamme de dizaines de nanomètres à quelques millimètres. De plus, la visualisation 3D des bulles volumétriques est reconstituée à partir des résultats de la tomographie aux rayons X.