



Multiscale modelling of transport properties for durability assessment of reinforced concrete in marine environment

Jack Atallah

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Par

Jack ATALLAH

Multiscale modelling of transport properties for durability assessment of reinforced concrete in marine environment

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Unité de recherche : GeM- Institut de recherche en génie civil et mécanique-UMR CNRS 6183

Rapporteurs avant soutenance :

Aveline DARQUENNES

Tulio HONORIO DE FARIA

Professeur des Universités, INSA Rennes

Chargé de recherche HDR, CEA Paris-Saclay

Composition du Jury :

Président :

Examineurs :

Alain SELLIER

Jos BROUWERS

Jean-François BARTHELEMY

(à préciser après la soutenance)

Professeur des Universités, Université Toulouse III

Professeur des Universités, Eindhoven University of Technology

Chercheur de l'UMR MCD (Cerema/UGE)

Directrice de thèse : Stéphanie BONNET

Encadrants de thèse : François BIGNONNET

Harifidy RANAIVOMANANA

Professeur des Universités, Nantes Université

Maître de conférences, Nantes Université

Maître de conférences, Nantes Université

“ No one can pass through life without leaving tracks behind, and those tracks may often be helpful to those coming after him in finding their way. ”

Robert Baden-Powell

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Chapter I

Introduction

I.1- Study Context and Problem Statement

Concrete is a fundamental material in the construction industry, accounting for 90% of the market [1], with an annual consumption reaching approximately 30 billion tons as of 2022 [2]. It ranks as the most consumed substance by humans after water [3]. The global demand for cement in construction has surged significantly. Producing Ordinary Portland Cement (OPC) involves mining limestone and manufacturing it, releasing substantial amounts of carbon dioxide. As of 2022, the cement industry is responsible for approximately 2.5 gigatons of CO₂ emissions annually, accounting for about 7% of total global CO₂ emissions [2]. This makes the cement industry the fourth largest contributor to global carbon emissions, following petroleum, coal, and natural gas.

Given the significant CO₂ footprint of cement production and the rapid increase in global cement demand, research has focused on developing alternative binders with lower carbon footprints. One approach is to substitute a part of the cement with other minerals, such as blast furnace slag, silica fume, and metakaolin. Blast furnace slag, in particular, has advantages: it reduces CO₂ emissions as it is a byproduct of the steelmaking industry [4], while decreasing the diffusion coefficient by refining the pore structure thus enhancing the reinforced concrete structure durability particularly in marine environments [5–7].

In marine environments, steel reinforced concrete (RC) structures are particularly vulnerable to deteriorating factors such as chloride ingress, which can lead to the corrosion of the steel reinforcement. This corrosion results in volumetric expansion of the steel, causing cracks and overall degradation of the concrete structure. The durability of concrete is closely linked to the evolution of its pore network, which in turn affects its mechanical strength and transport properties. This evolution is a complex process driven by cement hydration reactions and the resulting microstructure of the cement matrix. These hydration reactions depend significantly on the nature of the binder used in the concrete mix.

The degradation of concrete and its impact on material durability are critical scientific and industrial challenges in civil engineering. Despite advancements in ensuring the durability of various concrete compositions, the challenge of sustainable development in terms of design, formulation, and implementation remains a significant problem for both the scientific community and the construction industry. Enhancing concrete durability directly contributes to the reduction of CO₂ emissions by extending the service life of structures, thereby lowering the overall CO₂ emissions per year of service.

I.2- The DEMCOM project

This work is financed by an ANR DEMCOM project (DEMCOM ANR-20-CE22-0008-01), a multidisciplinary project that addresses the monitoring and durability of reinforced concrete structures, its life cycle assessment and life cycle cost. The aim is to create a new eco design method that will maximize service life while reducing the environmental impact and costs of reinforced concrete structures exposed to marine environment and monitored with resistivity probes. The methodological approach, described by the Figure 1 is the conducting line of the DEMCOM project.

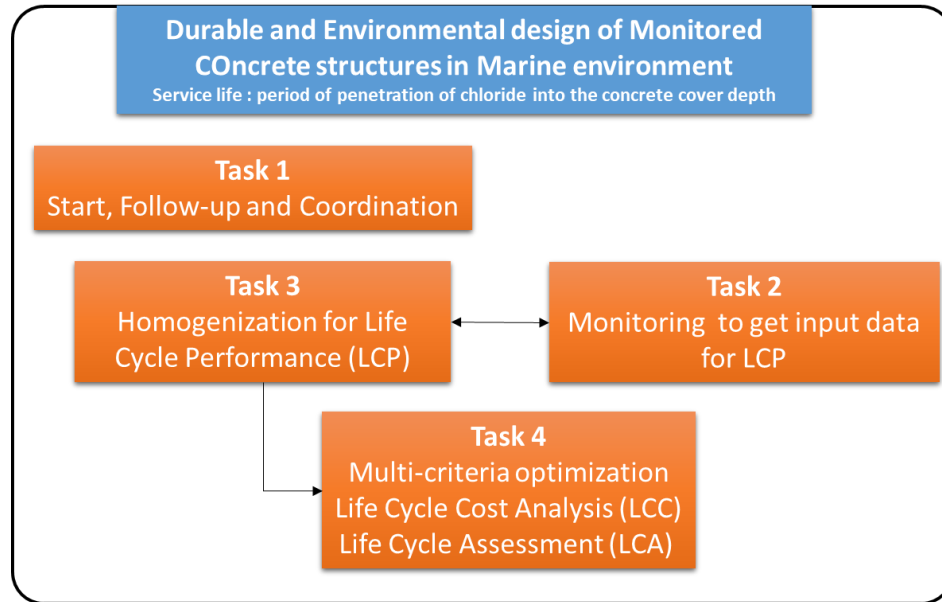


Figure 1: DEMCOM WPs interactions.

This PhD work is among two others thesis that are also part of the DEMCOM project. The articulation between the three thesis is explained as follows:

-Firstly, the present study deals with hydration properties and chloride profiles evolutions that are compared with non-destructive measurements performed in the PhD of Marie-Ange Eid at Université Gustave Eiffel.

- Secondly, from the modeling approach developed in this work, it can be possible to estimate the diffusion coefficient depending on the material composition which is considered as an input parameter in the durability model performed in the PhD of Hiyam DAHANI at Université Gustave Eiffel. This study couples LCA and LCC by using the same input of concrete mixture.

This thesis is part of WP3. The durability models dealing with chloride ingress have been not yet combined with LCA and this requires to include, as inputs parameters for both models, relevant and controlled technological parameters (concrete mix design, construction parameters) and environmental non-controlled parameters (meteorology, salinity...).

The integration of LCC & LCA with durability models thus faces a major issue related to the incompatibility of input data. The challenge is then to faithfully model concrete transport properties from concrete mix design to bridge this gap. The idea is to turn to multi-scale modelling that has indeed proved its ability to directly derive some concrete transport and mechanical properties from mix design parameters mostly for Portland cement [8–12]. The aim of this PhD is to study alternative binders incorporating industrial by-products, as blast furnace slag which is known for reducing the risk of corrosion [13–15].

I.3- Thesis objective

The purpose of this PhD work is to predict the transport properties of slag blended cementitious materials using a multiscale homogenization model that incorporates both a hydration model and a microstructural model (Figure 2). The work planned for the thesis in this document is divided into three main elements:

- 1) An appropriate hydration model to determine the evolution of the amount of each phase (various types of hydrates, anhydrous phases and pores) from concrete composition,
- 2) A morphological model to describe the microstructure and pore structure across different length scales,
- 3) Suitable homogenization schemes to successively upscale the macroscopic properties of interest from those of each phase at the microscopic scales.

To achieve this goal, a combination of models will be employed, starting with a well-developed hydration model that is based on the chemical reactions that occurs. Next, an appropriate microstructural model will be developed to describe the main aspects of the morphology of the microstructure of cement pastes and its development through the hydration process. Finally, a homogenization computation will be executed based on different schemes. The diffusion model created will then be validated with experimental results.

The hydration model provides the evolution of the hydrated phases through time, while the microstructural model provides the geometrical distribution of these phases. The focus of this work is to model the hydration of slag blended cement to gain insights into its behavior. The work is divided into two main parts: the hydration model adapted for the slag blended cement (Chapter II, III and IV), the morphological and the multiscale homogenization model (Chapter V, VI and VII).

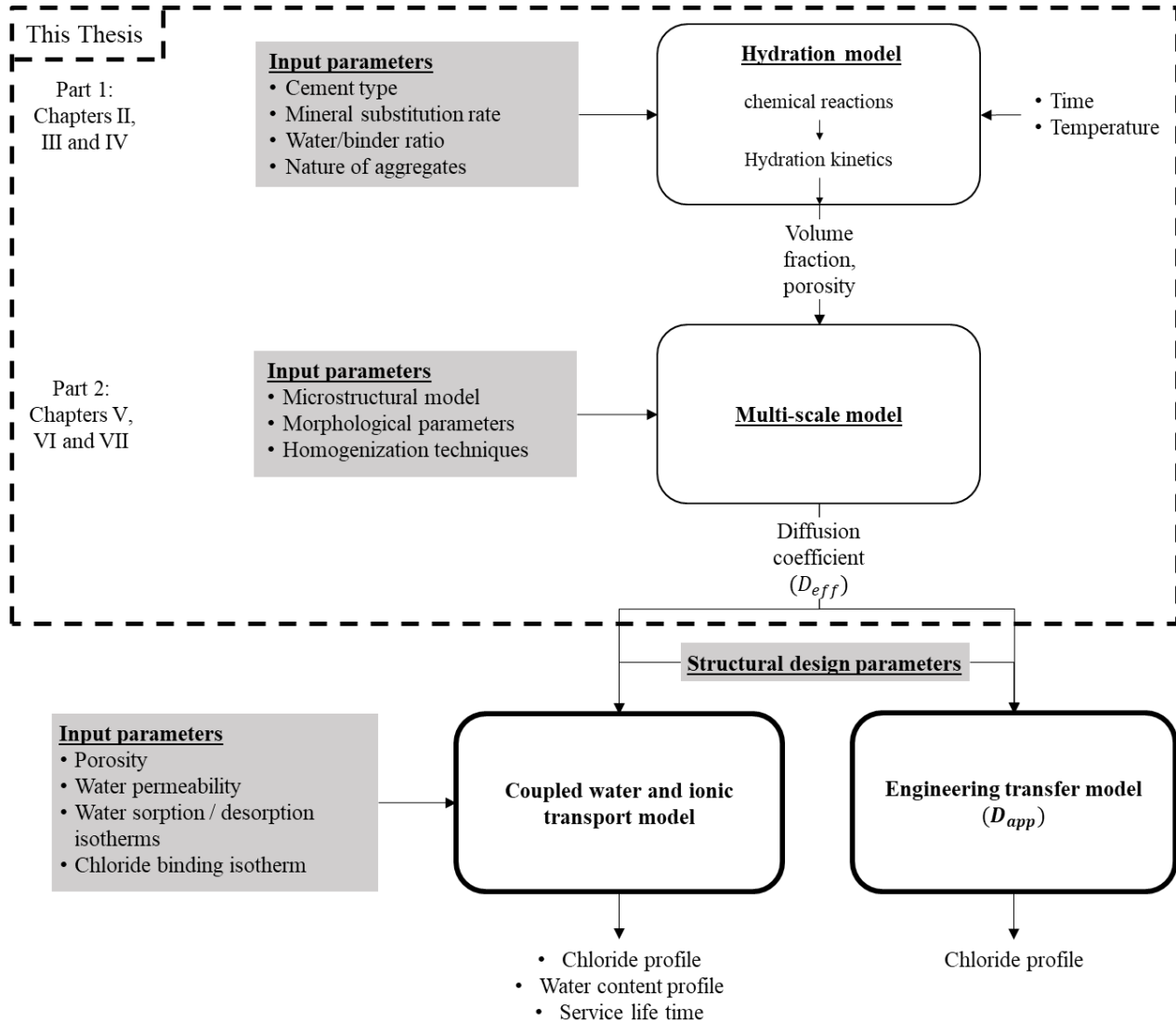


Figure 2: Flowchart of the models used by the WP3 of the DEMCOM project.

I.4- Outline of thesis

The thesis is structured into two main parts, each consisting of three chapters. The first part focuses on the hydration mechanisms of slag-blended cement, while the second part addresses the multiscale modeling of the effective diffusion coefficient. The detailed outline, as illustrated in Figure 3, is as follows:

Chapter I: Introduction: This introductory chapter establishes the context and significance of the study, emphasizing the importance of using slag blended cements. It also presents the DEMCOM project that this work is part of, while presenting the thesis objectives and outline.

Chapter II: Hydration reactions of slag blended cements: This chapter explore the chemical reactions involved in the hydration of slag blended cements. Hydration reactions of clinker phases are first reported. The discussion then shifts to the slag blended cement hydration reactions, detailing how these reactions

contribute to the overall properties of slag blended cementitious materials. A large part of the chapter is dedicated to a review of existing hydration models for slag blended cementitious materials. This includes analytical models for Ordinary Portland Cement and for slag blended cements along with numerical models. The benchmark section provides a summary of the models' characteristics, facilitating a comparison that aids in identifying the most effective modeling approaches.

Chapter III: Hydration kinetics for slag blended cements: this chapter focuses on the modeling of hydration kinetics in slag blended cements. First a review of existing models developed for OPC-based materials is addressed. The second part of the chapter is dedicated to the review of existing models developed for slag blended cements. This chapter identifies the limitations of existing models for long-term slag hydration kinetics. To address these gaps, a large experimental database is constructed, forming the basis for developing and validating a more accurate model tailored to the study's objectives. A new proposed model for slag hydration kinetics is developed and validated using this database. Its sensitivity to different variables is illustrated for various cases.

Chapter IV: Hydration combined model of slag blended cement: this chapter presents the development of a combined hydration model for slag blended cement. This model integrates both kinetics (explained in chapter III) and the chemical aspects (explained in chapter II), providing a framework for modeling the time dependent hydration process in slag blended cement. The chapter then moves on to various validation cases for the hydration model, demonstrating its accuracy and reliability. This includes comparing model predictions with experimental data and other established models, ensuring that the proposed combined hydration model can effectively represent the hydration process in slag blended cement under different conditions.

Chapter V: Microstructure properties of slag based cementitious materials: this chapter focuses on the multi-scale modeling of transport properties in cementitious materials. It begins with a detailed examination of the microstructure, particularly the hydrated phases, and specifically the calcium-silicate-hydrate (C-S-H) phases. The discussion on porosity covers the variations in porosity in different cement compositions and hydration states. The chapter also addresses the modeling of porosity, illustrating how it evolves during hydration, and considers the effects of slag addition on porosity characteristics. Additionally, it discusses specific surface area and connectivity, factors that significantly impact transport properties.

Chapter VI: Diffusive properties of slag blended cementitious materials: this chapter provides a comprehensive analysis of diffusion within cementitious materials, with a specific focus on slag blended cement. Initially, it establishes a theoretical foundation by discussing the general principles of diffusion. The discussion then advances to the mechanisms of diffusion in both saturated and unsaturated environments, emphasizing the variations caused by different marine environment. A critical distinction is made between apparent and effective diffusion coefficients, with a detailed review of the experimental methodologies used to measure these coefficients. The chapter further delves into analytical models that predict the diffusion mechanisms within cementitious materials. The conclusion of this chapter is a

comprehensive evaluation and classification of diffusion coefficients specific to slag-blended cement, based on an extensive compilation and analysis of experimental database, used in the next chapter to validate the multi-scale model.

Chapter VII: Multi-scale modeling of diffusion properties of cementitious materials: this chapter presents the theoretical and practical aspects of homogenization in cementitious materials. It begins with an in-depth exploration of homogenization theory and techniques, particularly those based on Eshelby's problem, and discusses their application in diffusion analysis. The Mori-Tanaka and self-consistent homogenization schemes, are analyzed to provide a comprehensive understanding of the process. The chapter also reviews some microstructure models for cementitious materials presented in the literature, providing a state-of-the-art assessment. A significant portion of the chapter is dedicated to the development of a two-scale homogenization model, detailing the methodology for incorporating slag substitution into an analytical multi-scale diffusion model. This model includes a comparative analysis and explores the impact of slag substitution on diffusion coefficients.

Chapter VIII: Conclusion and perspectives: the final chapter synthesizes the findings from the previous chapters, highlighting the significant contributions and advancements made in understanding and modeling the properties of slag blended cement. The chapter also outlines potential future research directions, proposing areas where further investigation could yield additional insights and improvements in the field.

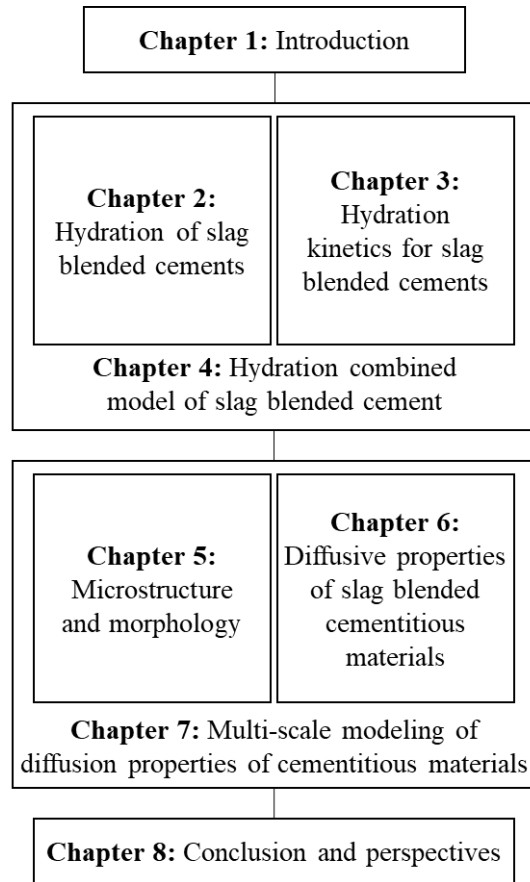


Figure 3: Thesis outline.

Chapter II

Hydration reactions of slag blended cements

II.1- Hydration reactions of slag blended cements

In the context of a comprehensive research initiative aiming at predicting the transport properties of concrete for marine structures based on a relevant description of the microstructure, the chapter centers on investigating the hydration processes of slag blended binders.

Due to both technical and environmental motivations, the use of clinker is progressively being supplanted by alternative materials. Blended cements, which are a mixture of clinker and other materials including blast-furnace slag, silica fume, and limestone, are used in engineering practice to reduce expenses [16, 17].

Considering the growing use of such composite cements in civil engineering applications, particularly for marine structures, it becomes imperative to accurately predict their hydration properties. This necessity emerges from the significant variation in the properties of the material depending on the initial mixture and conditions [18]. It is necessary to develop a comprehensive hydration model to correctly predict the properties' evolution.

The hydration modeling of slag blended cement materials, allows for the prediction of the evolution of microstructure in function of time based on formulation parameters. This modeling provides detailed insights into the volumetric fractions of various phases—unhydrated materials, hydrates, and pores—over time. These volumetric fractions are crucial inputs for the diffusion multi-scale model developed in Chapter VII.

This chapter provides a comprehensive literature review of Ordinary Portland Cement and slag hydration models in terms of chemical reactions. The chapter concludes with a benchmarking exercise designed to highlight these models, emphasizing their advantages and limitations.

II.1.1- Clinker phases and hydration reactions of Ordinary Portland Cements

Clinker is the fundamental component of industrial cements. It was first synthesized by Louis Vicat in 1818 [19]. Ordinary Portland Cement (also noted as CEM I – see Table 1) contains 98% clinker, which is used as the binder in most cement products. Clinker is produced by heating a mixture, typically consisting of about 80% limestone and 20% clay minerals, to approximately 1450°C in a furnace. Clinker, when incorporated with gypsum and finely grounded produces cement. Gypsum is added as a set regulator, preventing the cement from setting too quickly and allowing adequate time for application.

Main types	Notation of the products (types of common cement)	Composition (percentage by mass ^a)											
		Main constituents										Minor additional constituents	
		Clinker	Blast-furnace slag	Silica fume	Pozzolana		Fly ash		Burnt shale	Limestone			
					natural	natural calcined	siliceous	calcareous		L	LL		
			K	S	D ^b	P	Q	V	W	T	L	LL	
CEM I	Portland cement	CEM I	95-100	-	-	-	-	-	-	-	-	-	0-5
	Portland-slag cement	CEM II/A-S	80-94	6-20	-	-	-	-	-	-	-	-	0-5
		CEM II/B-S	65-79	21-35	-	-	-	-	-	-	-	-	0-5
CEM II	Portland-composite cement ^b	CEM II/A-M	80-88	←—————→				12-20	—————→				0-5
		CEM II/B-M	65-79	←—————→				21-35	—————→				0-5
CEM III	Blast furnace cement	CEM III/A	35-64	36-65	-	-	-	-	-	-	-	-	0-5
		CEM III/B	20-34	66-80	-	-	-	-	-	-	-	-	0-5
		CEM III/C	5-19	81-95	-	-	-	-	-	-	-	-	-

a)The values in the table refer to the sum of the main and minor additional constituents.

b)In Portland-composite cements CEM II/A-M and CEM II/B-M the main constituents other than clinker shall be declared by designation of the cement.

Table 1: Extract of Composition and notation of common cements according to the standard NF EN 197-1 (Avril 2012)[20].

Cement is constituted by different chemical elements (oxides) (presented in Table 2), whose quantities vary depending on both type and amount of mineral additions [20] .

Chemical formula	Cement chemistry notation	Name	Range in Clinker (%)	Range in Slag (%)
CaO	C	Calcium oxide, or lime	60-67%	30-50%
SiO ₂	S	Silicon dioxide, or silica	17-25%	28-38%
Al ₂ O ₃	A	Aluminum oxide, or alumina	3-8%	8-15%
Fe ₂ O ₃	F	Iron oxide, or rust	0.5-6%	0.5-1.5%
TiO ₂	T	Titanium dioxide, or Titania	<1%	<1%
MgO	M	Magnesium oxide, or periclase	0.5-4%	2-5%
K ₂ O	K	Potassium oxide	0.2-1.5%	<1%
Na ₂ O	N	Sodium oxide	0.1-1%	<0.5%
H ₂ O	H	Water	-	-
CO ₂	c	Carbon dioxide	-	-
SO ₃	$\bar{S}$	Sulfur trioxide	1-3%	0.5-2.5%
P ₂ O ₅	P	Phosphorus hemi-pentoxide	<0.5%	<0.5%

Table 2: Abbreviations used for cement chemistry oxides.

In clinker, oxides are combined into four crystalline phases, which are presented in Table 3 [21].

Clinker Phases	Chemical Formula	Cement chemistry Notation	Molar Mass (g/mol)	Density (g/cm ³)	Molar volume (cm ³ /mol)
Tricalcium silicate	Ca ₃ SiO ₅	C ₃ S	228	3.15	72.4
Dicalcium silicate	Ca ₂ SiO ₄	C ₂ S	172	3.28	52.4
Tricalcium aluminate	Ca ₃ Al ₂ O ₅	C ₃ A	486	3.03	89.2
Tetra-calcium aluminoferrite	Ca ₄ Al ₂ O ₁₀ Fe ₂	C ₄ AF	270	3.73	130.3
Gypsum	CaSO ₄ 2H ₂ O	C $\bar{S}$ H ₂	172	2.32	74.1

Table 3: Different clinker phases and properties [21].

- Alite or tricalcium silicate is responsible for the early strength development. 70% of C₃S reacts within the first 28 days of hydration. It represents 40%-70% of the mass of clinker.
- Belite or dicalcium silicate is responsible for the late strength development. 30% of C₂S reacts within the first 28 days of hydration. It represents 20%-40% of the mass of clinker.

- Tricalcium aluminate does not really contributes to the strength of the cement. This compound is responsible for the early high heat generation in hydration (rapid hydration) thus for the setting time of cement.
- C_4AF - Ferrite or tetra calcium alumina ferrite - $4CaO, Al_2O_3Fe_2O_3$ does not also contribute significantly to strength. It gives the cement its color [22].
- Gypsum - $CaSO_4 \cdot 2H_2O$ is a key ingredient in cement, acts as a set regulator by controlling the hydration rate and preventing flash setting during the early stages of cement hydration. Bogue's calculation does not account for the presence of gypsum, as it assumes that other phases react fully without considering the added gypsum used.

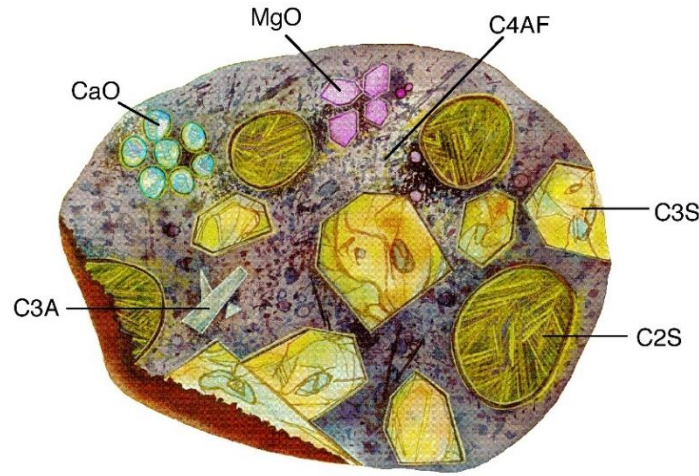


Figure 4: Representation of clinker phases from Fahlman (2018) [23].

The most widely applied method to estimate the mineralogic composition of clinker from the weight percentage x_i of oxides is the Bogue's calculation [24] as shown in equations (1)-(4). Although, estimated amounts of individual phases derived by the Bogue calculation are considered consistent with experimental results, the Bogue's estimation does not account for other phases and factors that may also play a significant role in determining the final properties of the cement [24].

$$x_{C_3S} = 4.07 x_C - (7.60 x_S + 6.72 x_A + 1.43 x_F + 2.85 x_{\bar{S}}) \quad (1)$$

$$x_{C_2S} = 2.87 x_S - 0.754 x_{C_3S} \quad (2)$$

$$x_{C_3A} = 2.65 x_A - 1.69 x_F \quad (3)$$

$$x_{C_4AF} = 3.04 x_F \quad (4)$$

The presence of silica in C_3S and C_2S makes them responsible for the strength of cement. They produce calcium hydroxide (CH) and calcium silicate hydrate (CSH) when mixed with water. C_3A can cause cracks, like shrinkage cracks, due to the high temperature release [25]. As result a 4%-6% gypsum must be added to attack C_3A and regulate the setting time of cement. When mixed with water and gypsum C_3A produces ettringite and monosulfate hydrate.

The process known as "hydration" encompasses the series of chemical reactions that occur when anhydrous cement comes into contact with water, leading to the formation of a cementitious matrix. This matrix gradually hardens, significantly contributing to the mechanical strength of the structure. The main products of hydration, along with their chemical formulas, are detailed in Table 4. Upon the introduction of water to (slag-blended) cement, a layer of hydrates begins to form on the surface of the anhydrous grains, facilitating a cohesive bond among the particles. As hydration progresses, this hydrate layer thickens and reduces the space initially occupied by water over time. A study by Day et al. [26] has shown a notable decrease in porosity accessible to water in pastes (measured by drying the sample at 105°C) by 5% between seven days and three months of hydration. Kocaba [27] reported a reduction in porosity from 56% (initial porosity) to 43% in a CEM I cement paste. This reduction in porosity is influenced by the rate of hydration and the characteristics of the forming phases.

Abbreviation	chemical formula	Name	Density (g/cm ³)	Molar Mass (g/mol)
CH	Ca(OH) ₂ or CaO · H ₂ O	Calcium hydroxide	2.24	74.1
C-S-H	$\hat{a}$ CaO · SiO ₂ · g H ₂ O	Calcium silicate hydrate		
C-S-A-H	$\hat{a}$ CaO · SiO ₂ · $\hat{b}$ Al ₂ O ₃ · g H ₂ O	Calcium aluminate hydrate		
AFt	C ₆ (A,Fe) $\bar{S}$ ₃ H ₃₂	Calcium trisulfoaluminate hydrate, or ettringite	1.78	1255.3
AFm	C ₄ (A,Fe) $\bar{S}$ H ₁₂	Calcium monosulfoaluminate	1.98	634.5
Cc	CaCO ₃	Calcium carbonate	2.71	100.1
HT	M ₅ AH ₁₃	Hydrotalcite	1.80	645.5
HG	C ₆ AFS ₂ H ₈	Hydrogarnet	2.24	1042.4
AH	C ₄ AH ₁₃	Tetracalcium	1.92	668.4
monoc	Ca ₄ Al ₂ (CO ₃)(OH) ₁₂ · 5H ₂ O	Monocarboaluminate de calcium	1.98	564.5
FH ₃	FeH ₃ O ₃	Iron hydroxide	4.25	106.87
MH	M _g (OH) ₂	Brucite	2.39	58.32

Note: To avoid repetition, This table also encompasses the hydration products formed in slag-blended systems, as the inclusion of slag in the cement matrix leads to the formation of similar products, with the appearance of additional phases specific to slag hydration

Table 4: Different slag blended cement hydration products and their chemical formulas [21].

Upon mixing with water, cement hydration initiates immediately, and the hydration reaction starts, which is exothermic, releasing heat in the process. This complex reaction is influenced by different factors [28], including:

- The composition of the cement and the chemical composition within the phases,
- The distribution of particle sizes,
- The water to binder ratio,
- The curing parameters (temperature, availability of external water/solution,...)
- The addition of chemical admixtures, among others.

Each of these factors plays a significant role in determining the rate and extent of the hydration process, ultimately affecting the final properties of the hardened cement paste.

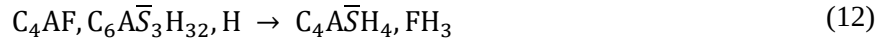
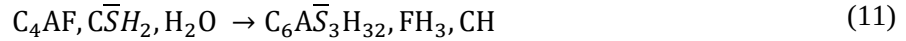
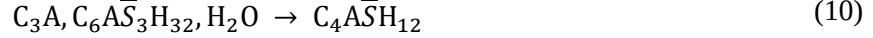
For later use, we define α as the hydration degree of the CEM I, α_i as the hydration degree of the CEM I phases ($i \in C_3S, C_2S, C_3A, C_4AF$ or *gypsum*). To calculate the specific hydration degree of an anhydrous phase, the following formula is employed:

$$\alpha_i = \frac{m_{initial\ anhydrous} - m_{anhydrous\ at\ time\ t}}{m_{initial\ anhydrous}} \quad (5)$$

Here, m represents the mass of the considered phase both initially and at a specific time t . We also defines α as the total hydration degree of the clinker calculated as:

$$\alpha = \frac{\sum_i \alpha_i m_i}{\sum_i m_i} \quad (6)$$

In general, the dissolution of the CEM I phases leads to these transformations that happen simultaneously but at different rates:



It is important to acknowledge that the depiction provided here is an idealization. Various researchers interpret the hydration reactions of cement differently [29–31], see section II.2.1-. This variation can arise from differing perspectives on the chemical composition of the hydration products, which influences their nature, as well as from their behavior during the hydration process. These inconsistencies highlight the complexity of hydration reactions and underscore the need for a nuanced understanding of the various factors that govern these processes in cement chemistry.

II.1.2- Blast Furnace Slag phases and hydration reactions

Blast furnace slag (BFS) is a by-product from the steelmaking industry, generated during the ironmaking production process as iron oxides are segregated from the ore's inert gangue [32] (Figure 5). Its valorization preserves fundamental raw materials and energy sources and, contribute to environmental protection [33].

The multiphase hydration model applied in this work is expanded in Chapter VII to include cement combined with ground granulated blast-furnace slag (GGBFS).

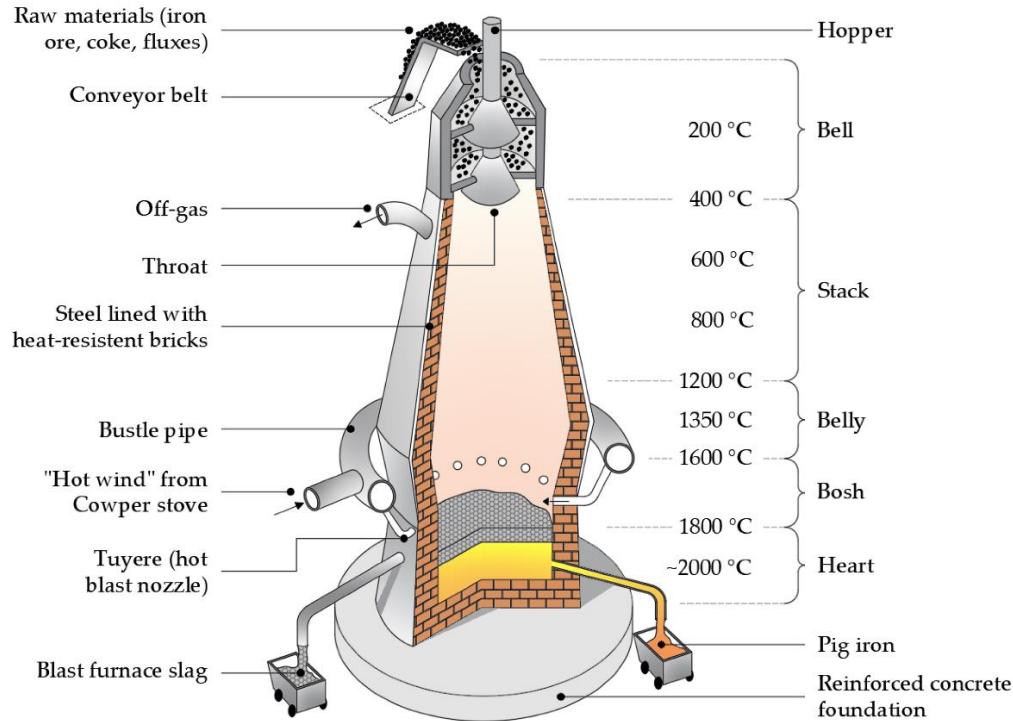


Figure 5: Schematic representation of the blast furnace [34].

Immediately after exiting the blast furnace, the slag undergoes rapid cooling, typically through granulation (spraying with pressurized water jets), to maximize the formation of a glassy phase with latent hydraulic properties. This slag is subsequently grinded, either together with or separate from CEM I. For the utilization of blast furnace granulated slag as a binding agent, it must be finely ground (Figure 6). According to several studies [35, 36], the slags are milled to a specific surface area of 250 to 400 m²/kg or more. As per EN 15167-1:2006 [37], the slags should exhibit a specific surface area of no less than 275 m²/kg. Yet, excessive grinding, while beneficial for slag activity, tends to increase its water demand [38, 39]. Therefore, for slags from different sources, it is imperative to identify the optimal slag dispersity that ensures the required water demand and reactivity.

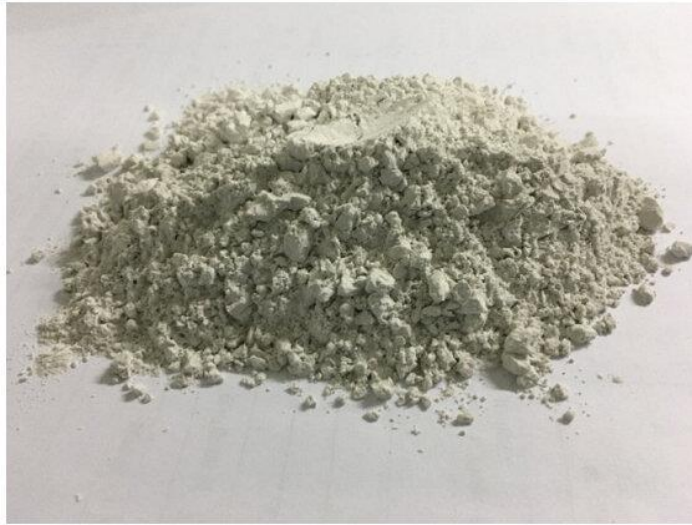


Figure 6: Granulated ground blast furnace slag [40].

Despite differing origins, slag and CEM I share similar primary oxide compositions [41]. Chemically speaking, slag is a mixture of metal oxides and silicon dioxide (oxides C, S, A, M, $\bar{S}$ and F; see Table 2). However, slag can contain metal sulfides and elemental metals. The content of SiO_2 , Al_2O_3 , and MgO is higher in slag than in Portland cement, but the content of CaO is lower [42]. Slag is composed of two general types of phases: crystalline and amorphous ones. Reaction may occur with the amorphous part only, while the crystalline part remains inactive. The crystalline phase of the slag may predominantly contain minerals such as melilite ($\text{Ca}_2(\text{Al,Mg})\text{Si}_2\text{O}_7$), gehlenite ($2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$), merwinite ($3\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2$), akermanite ($2\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2$), and monticellite ($\text{CaO}\cdot\text{MgO}\cdot\text{SiO}_2$), each presenting varying degrees of crystallinity [43, 44].

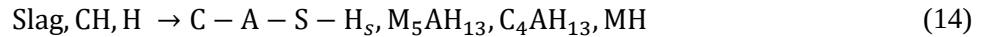
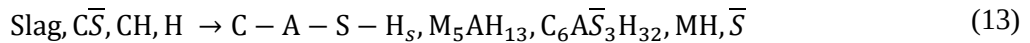
As mentioned above, blast furnace slag has latent hydraulic properties due to its amorphous glassy structure [45]. Generally, slag reacts for a brief period with water and releases calcium ions into the solution. This reaction stops quickly due to the creation of a water-impermeable layer on the surface of slag particles [46]. This reaction unfolds too sluggishly for practical application, necessitating activation, predominantly through blending with Portland cement. The hydration process of slag in blended cements is notably enhanced by the hydration of portland cement (PC), which releases $\text{Ca}(\text{OH})_2$ into the poral solution, subsequently serving as an activator for the slag component [47, 48]. Specifically, portlandite influences the slag hydration in two critical ways: initially, its chemical equilibrium at elevated pH facilitates the dissolution of the amorphous phases within the slag, thereby increasing its reactive surface area. Subsequently, calcium hydroxide contributes essential calcium ions, which are requisite for the synthesis of calcium silicate hydrate (C-S-A-H) structures, compensating for the inherent calcium deficiency in slag. In general, the proportion of slag in slag blended cement can vary between 30% and 90% [49]. During hydration, blast furnace slag reacts with alkali hydroxides, followed by reaction with

calcium hydroxide released by Portland clinker, resulting in the formation of calcium silicate hydrates (C-(A)-S-H), ettringite, and other aluminates [50, 51].

As a result, the combination of slag and Portland cement can result in a cement group with high reactivity and performance. The hydration process of blended cements is quite complex because both constituents react with water and their hydration processes interact with each other. Hydration reactions of slag occur at a slower rate than those of CEM I, and the enhancement of concrete's mechanical strength continues over an extended period. Slag can also enhance the concrete's microstructure and chloride resistance [50, 52–54].

While CEM I and slag hydration reactions share common products such as C-S-A-H, calcium monosulfate aluminate (AFm phases), and ettringite, the reaction pathways and outcomes can differ significantly [55–59]. Slag alone, due to its lower calcium content [60], is unable to form portlandite or C-S-A-H with a CaO/SiO₂ ratio of 1.8 (ratio of CaO/SiO₂ in CEM I). Research has shown that portlandite persists even after extended hydration periods, indicating a continuing reaction with slag to adjust the C-S-A-H composition [58, 61]. Taylor et al. [61] reported the presence of portlandite after 20 years of hydration in cements with slag contents up to 90%, where the CaO/SiO₂ ratio of the cement was 1.2. Similarly, Luke et al. [58] found that a cement paste containing 30% slag had a portlandite content of 18%, in contrast to 30% for pure Portland cement. This outcome is consistent with the initial cement's CaO/SiO₂ ratio of 2.4. These findings highlight the long-term influence of slag on the hydration products of cement, altering the long-term presence of portlandite. Harrison's [62] work further corroborates these observations, validating that the quantity of calcium hydroxide (CH) produced in cement containing slag is lower than that in a pure Portland cement mixture.

Meanwhile, while the slag has a chemical composition similar to the CEM I, the hydration reactions are not the same. Some main products are created by the same reactions such as calcium monosulfate and ettringite, but other products are also created mostly the calcium aluminate hydrate formed by this reaction:



As noticed, some hydration reactions of slag require the presence of portlandite CH as indicated before, highlighting the interdependence of slag and CEM I in blended cement mixtures.

The presence of aluminum in the interstitial solution from slag can lead to its incorporation into C-S-H, transforming it into C-S-A-H. These hydration reactions have been treated from different perspectives through literature, depending on different hypothesis and experimental analysis. The chemical composition of CEM I and slag elucidates why similar primary hydrates to those found in Portland cement are observed: C-S-A-H, portlandite, AFt phases, and AFm phases [63]. However, it is notable that slags

typically contain higher levels of aluminum, silicon, and magnesium, and lower levels of calcium. This compositional difference leads to a greater quantity of hydrotalcite and C-S-A-H with a lower Ca/Si ratio and a higher Al/Si ratio, as well as potential dissolution of portlandite [64, 51, 65].

It is important to note that, the binding phase of cementitious materials is primarily composed of Calcium-Silicate-Hydrate (C-S-H) or Calcium-Alumina-silica-hydrate (C-S-A-H) (in case of a slag substitution), with variable stoichiometric coefficient depending on the author [66]. Therefore, in Table 4, the stoichiometric coefficients of C-S-A-H are denoted as $\hat{a}$, $\hat{b}$, and g to account for this variability. These ratios are influenced by different factors, including temperature changes (which modify equilibrium constants) and the calcium and silicon concentration in the solution, determined by the solubility constants. An increase in calcium concentration (or a decrease in silicon concentration) results in a higher Ca/Si ratio in C-S-A-H, which typically ranges between 0.7 and 1.8. The limits of this range are dictated by the solubility of amorphous silica and portlandite, respectively [67].

The notable fluctuations in the Ca/Si ratio can be attributed to two main factors: firstly, the existence of at least three distinct C-S-H phases [$\text{Ca}_4\text{H}_4\text{Si}_5\text{O}_{16}$, $\text{Ca}_2\text{H}_2\text{Si}_2\text{O}_7$, $\text{Ca}_6(\text{HSi}_2\text{O}_7)_2(\text{OH})_2$] with other C-S-A-H phases that incorporates Aluminum addition when slag is present, each with its own solubility; and secondly, the process of calcium and silicon adsorption or desorption on the surface of these C-S-H / C-S-A-H phases [68]. Silicon Nuclear Magnetic Resonance (NMR) analyses support this structural characterization of C-S-H/ C-S-A-H, as illustrated in Figure 7. This figure effectively demonstrates how changes in the calcium-to-silicon (C/S) ratio influence the length of C-S-H/ C-S-A-H chains [69–72]. Specifically, as the C/S ratio increases, the analyses show a reduction in C-S-H/ C-S-A-H chain length. This observation is significant as it highlights the impact of the chemical composition on the microstructural properties of C-S-H/ C-S-A-H, which in turn can affect the material's overall mechanical properties and durability.

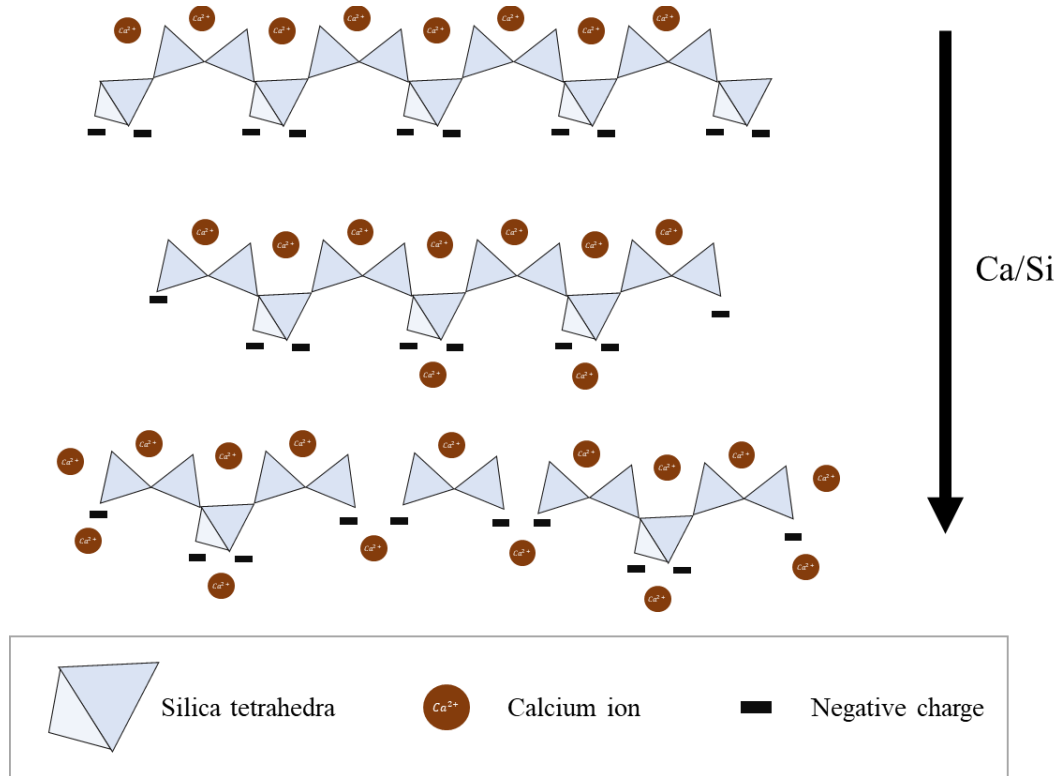


Figure 7: Simplified C-S-H structure based on C/S ratio inspired by [73].

The reactivity of slag in slag-blended cement is a crucial factor that directly influences the material's performance, notably its mechanical properties and durability. This reactivity is determined by a complex interplay of four main factors: chemical composition, slag processing methods, geometrical properties of the slag particles, and the parameters involved in mixing the slag with cement as shown in Figure 8.

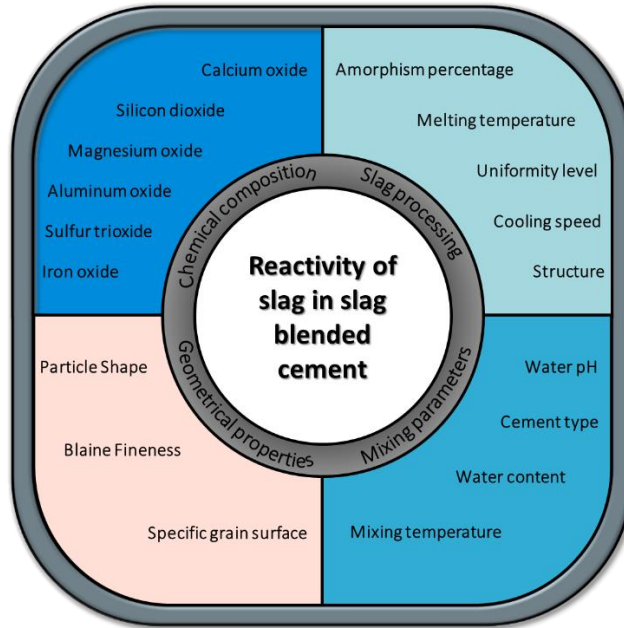


Figure 8: Factors influencing the reactivity of slag in slag blended cement.

Chemically, the reactivity hinges on the presence and proportions of primary oxides such as Silicon dioxide (SiO_2), Calcium oxide (CaO), and Aluminum oxide (Al_2O_3) (Table 2). These oxides are pivotal in dictating the slag's hydraulic properties, influencing its ability to form calcium silicate hydrate that mainly governs the material's strength [74]. The slag's manufacturing, especially the rate of cooling, significantly impacts its crystallinity. A rapid cooling of slag during its manufacturing leads to a glassy structure that is more reactive due to its increased surface area and amorphous nature, which significantly enhances its chemical reactivity and potential for hydration when used as a cementitious material [75]. Furthermore, the physical properties of slag, such as particle size and shape, significantly influence the kinetics of the hydration process. Specifically, when slag exhibits higher fineness (Blaine fineness), its increased surface area allows for quicker hydration reactions compared to slag with lower fineness. Additionally, the conditions under which slag is mixed with cement, such as mixing temperature and water pH, also play crucial roles. For example, higher curing temperatures accelerate the hydration process by increasing the rate of chemical reactions, facilitating faster setting and strength development of the cement-slag mixture [76, 77]. Properly utilizing these parameters enhances the efficiency of cementitious materials by maximizing slag's role tailored to specific needs [78].

For later use, we define γ as the hydration degree of slag, and λ the substitution ratio of slag in the binder by mass.

II.2- Existing hydration models for slag blended cementitious materials

While the hydration processes of Ordinary Portland Cements are widely studied in literature, studies on slag-blended cements, although available, often place less emphasis on the in-depth analysis of the

microstructural development and specific interactions within slag-based materials. The hydration of slag has to be investigated in terms of chemical reactions but also in terms of kinetics.

In a study involving slag-blended cement hydration modeling, it is essential to understand that each model possesses its own specific characteristics and limitations. These characteristics might be chemo-physical, such as the chemical composition of the output phases, or technical, such as the model execution time. Choosing a hydration model is a critical step that should precede the formulation of a multiscale model of cementitious material properties. Therefore, a benchmark of existing models is carried out to select the one best suited for the developments of Chapter VII.

Several hydration models based on microstructure modeling have been proposed previously (HYMOSTRUCT3D [79], CEMHYD3D [80], μ IC [81] ...). These models provide a relevant description of the microstructure evolution during hardening but require a long computing time. Here lies the importance of analytical models, that provide reliable results in a very fast computational time. Additionally, models developed by Powers [82] and Tennis and Jennings [83] designed for OPC are also included for comparison purposes on Ordinary Portland Cement.

The different models investigated hereafter are:

- Powers' model [82],
- Tennis and Jennings's model [83],
- Chen & Brouwers' models [51, 65, 84],
- Kolani's model [6],
- CEMGEMS' model [85, 86],
- VCCTL's model [87],

Note that several other slag blended cement hydration models have been proposed by Stephant [88], Merzouki [89], Königsberger [66], Kinomura [90], Elakneswaran [91], Thomas [92], Phreeqc [93], Ali Ahmad [94]. These more recent models are promising but have not been treated in this benchmark. Some of these models are computationally time demanding, which makes them less practical for this study's scope. Additionally, certain models are complex to reprogram or adapt to the specific parameters needed for this research, limiting their applicability.

The section is organized as follows: the selected models are presented in sections II.2.1-, II.2.2-and II.2.3-. After that, they are implemented and compared to experimental data in section II.3-.

The benchmarked models are detailed below, in order to assess their reliability along with other criteria such as computational time and physical input parameters (consideration of temperature, curing conditions, oxides composition of binders). In terms of output data, phases quantities will be compared, especially the portlandite formation that can be quantified experimentally with a good reliability.

Powers' model [82] is applied for the Ordinary Portland Cement pastes hydration only. Tennis & Jennings' model [83] improves on Powers model, by taking into consideration time and further phases details. It is also non-applicable to slag blended cement.

Chen & Brouwers' analytical model [51, 65, 84] is based on chemical balance equations between oxides from OPC and slag and hydrated products through stoichiometric considerations. It does not offer a proper kinetic modeling; therefore, needed to be coupled with a kinetic model such as offered in Meinhard [21] or Mounanga [22].

Kolani's model [6] is an iterative numerical model, with relatively fast results, giving more details such as kinetics and heat flux.

CEMGEMS [85] is a fast-numerical model, but does not provide time depending results except when coupled with a built-in modified Parrott and Killoh's model, and gives promising results.

VCCTL [87] is a numerical model based on the CEMHYD3D system widely used in literature but has a long computation time.

II.2.1- Analytical models for Ordinary Portland Cement

II.2.1.1- Powers' Model

Powers' model [82] is a simplified model involving only three different phases: the hydration products, the anhydrous cement and capillary pores. Different models found in the literature are based on Powers' model with account for different cement additives (such as slag [88], fly ash [95] ...). Because of the limitations of Power's model to detail the variety of hydrated phases formed by the slag hydration, it is only studied here to be taken as a reference when dealing with hydration of cement.

The cement, water and hydration products quantity evolve during the hydration process depending on the initial water to cement ratio (w/c) as well as the curing conditions. The advancement of the hydration reaction is described using the mass ratio of hydrated cement to initial anhydrous cement, called hydration degree (α).

The volume fractions of the anhydrous cement, hydration products and capillary pores are calculated using the following formulas:

$$f_a = \frac{1 - \alpha}{1 + \frac{\rho_a w}{c}} \quad (15)$$

$$f_h = \frac{k_h \alpha}{1 + \rho_a w/c} \quad (16)$$

$$f_{cp} = \frac{\rho_a w/c + (1 - k_h)\alpha}{1 + \rho_a w/c} \quad (17)$$

where:

f_a : volume fraction of anhydrous cement [m^3/m^3 of material],

f_h : volume fraction of hydration products [m^3/m^3 of material],

f_{cp} : volume fraction of capillary pores [m^3/m^3 of material],

ρ_a : density of anhydrous cement (taken equal to 3.13 [-]),

k_h : volume of produced hydrates (taken equal to 2.13 [-]).

The curing conditions impose the determination of a maximum degree α , called α_{max} , that can be reached:

1. In absence of water exchange with the environment, one of the reactants is depleted. The maximum degree of α is given by Achour [9]:

$$\alpha_{max} = \frac{w/c}{k_w/\rho_a} \quad \text{if } w/c \leq k_w/\rho_a \quad (18)$$

Where $k_w/\rho_a \simeq 0.42$; otherwise α_{max} is taken equal to 1.

2. When external water can be supplied from the environment, either the cement is depleted, or all the space is filled with hydration products, the maximum degree of α in this case is:

$$\alpha_{max} = \frac{\rho_a w/c}{k_h - 1} \quad \text{if } \frac{w}{c} \leq (k_h - 1)/\rho_a \quad (19)$$

Where $(k_h - 1)/\rho_a \simeq 0.36$; otherwise, it α_{max} taken equal to 1.

The following figures illustrate the volume fractions determined for different w/c ratios, according to equations (15)-(17) and (19):

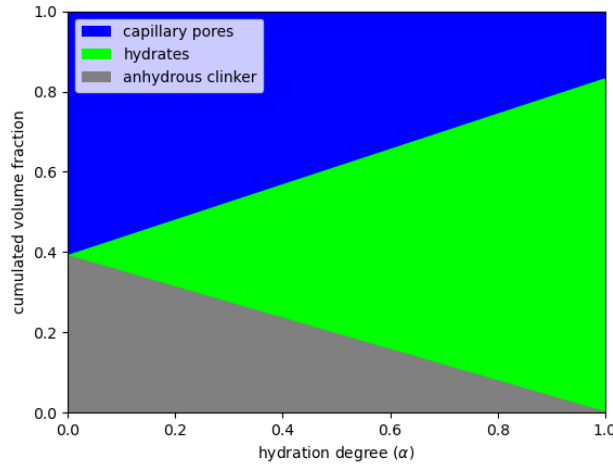


Figure 9: Volume fraction for $w/c=0.5$ for Powers' model.

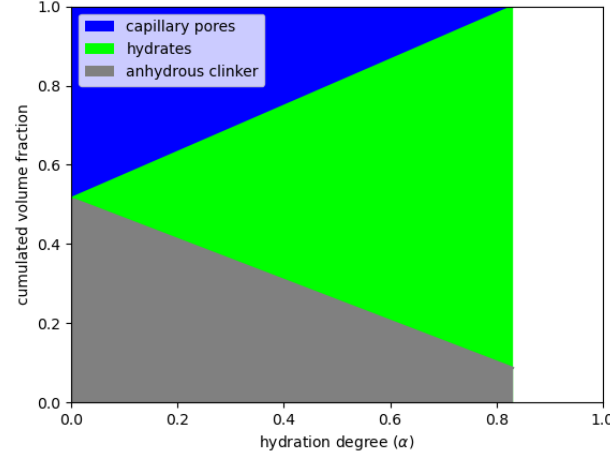


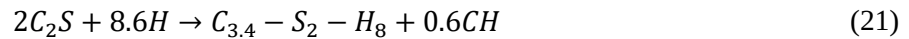
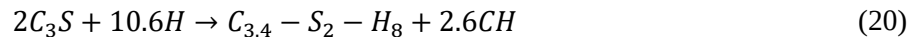
Figure 10: Volume fraction for $w/c=0.3$ for Powers' model. Max hydration degree is determined by (19) due to sealed curing conditions.

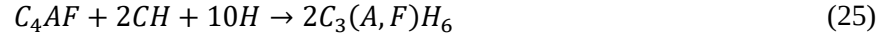
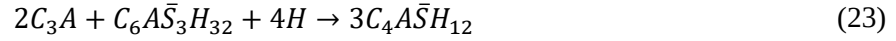
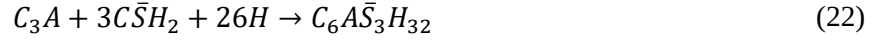
II.2.1.2- Tennis and Jennings' model

Tennis and Jennings's model [83] is a hydration model based on chemical reactions more detailed than Power's model. It distinguishes the anhydrous clinker phases (Alite, Belite, Aluminate and Ferrite), gypsum and the various hydration products phases (C-S-H, hydrogarnet, CH, AFm, Aft...). It also studies the kinetics of the reaction based on Avrami's equations for each phase as provided by Taylor [96]. These equations describe the kinetics of the hydration of the different cement phases. The model is based on the stoichiometric reactions for the hydration of the principal phases of clinker: C_3S , C_3A , C_2S and C_4AF .

The drawback of this model lies in the hypothesis that all the ettringite will react to form monosulfate, even though experimentally, it was proven that some ettringite is found at the end of the hydration process [97]. Another problematic point is the Bogue [24] calculation, converting the oxides present in the clinker to the clinker phases, which is only an approximation and doesn't provide exact values [98, 99]. Further, according to the authors themselves, Avrami equations are too simplistic to describe finely the hydration kinetics of cement paste.

The hydration reactions used in this model are:





The first two equations are responsible for the formation of the C-S-H. The third one is the main reaction of C_3A with gypsum to form ettringite. The rest of the C_3A reacts to form monosulfoaluminates. After all the ettringite is consumed the fifth equation occurs. At last, C_4AF reacts to form hydrogarnet.

The rates of the reactions assumed for the model are approximations based on Avrami equations of the form:

$$\alpha_i = 1 - e^{-(a_i(t-b_i)^{c_i})} \quad (26)$$

With i the different clinker phases, a_i , b_i and c_i the Avrami's coefficient determined empirically for a specific Portland cement [100] given in Table 5 below [96]:

Compound i	a	b	c
C_3S	0.70	0.90	0.25
C_2S	0.12	0.00	0.46
C_3A	0.77	0.90	0.28
C_4AF	0.55	0.90	0.26

Table 5: Parameters of Avrami's equation determined by Taylor [96].

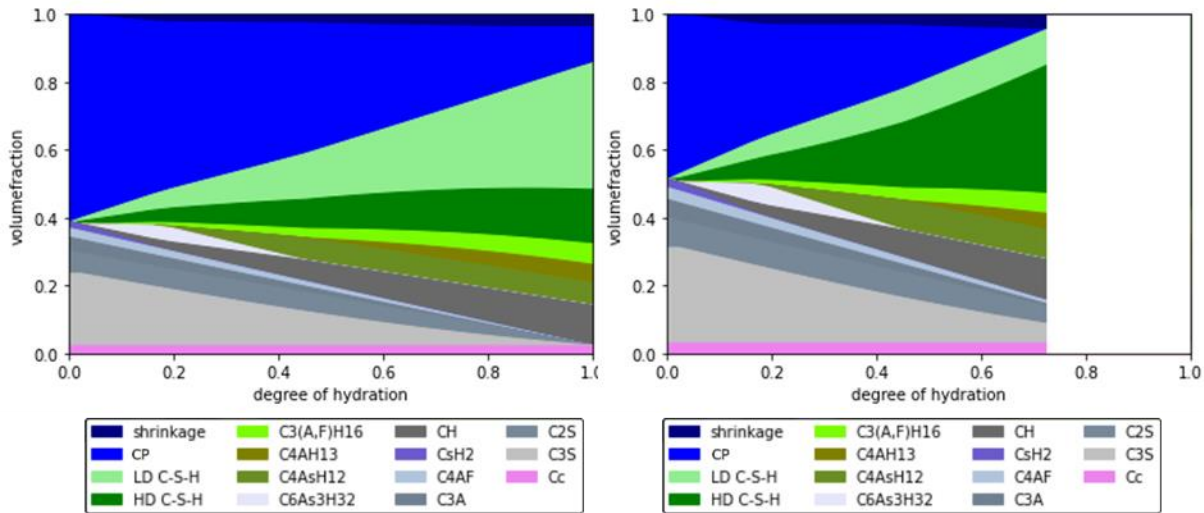


Figure 11: Volume fraction for Tennis and Jennings' model for $w/b=0.5$ (left) and 0.3 (right) respectively (sealed condition).

This model predicts the volume fractions of various compounds. It also quantifies the porosity (CP), partitioning it into capillary porosity and C-S-H porosity. It further distinguishes different C-S-H types (high-density C-S-H (HD C-S-H) and low-density C-S-H (LD C-S-H)). It also calculates the chemical shrinkage and can be used to compute physical properties of the cement.

It is worth precising that this model is only appropriate to the OPC cement hydration computation. It will serve as a reference for further models' validation in the case without slag substitution.

II.2.2- Analytical model for slag blended cement

Chen & Brouwers' model. Chen & Brouwers [51, 64] proposed three different models for the hydration of the pure clinker and slag blended cement. These models are based purely on the chemical reactions and stoichiometric calculations. The authors have considered different hypothesis for each model.

Starting with the initial oxide compositions and their proportions in the mixture, the hydration of the two main constituents (clinker and slag) is investigated separately, and then established considering the interaction of the hydration products. A mixture of the products of both Portland cement's hydration and slag's hydration is to form. The amount of CH formed by the Portland cement hydration is partially consumed by the slag hydration (Pietersen and Bijen, 1994 [101] ; Regourd, 1980 [102] ; Richardson and Groves, 1992 [69]).

A specific attention is payed to C-S-A-H whose composition varies depending on its calcium to silicon C/S ratio and aluminum to silicon ratio A/S. The three different models proposed for slag-blended cement are based on stoichiometry calculations, mainly to determine the C/S and the A/S ratios in the C-S-A-H, which impact the stoichiometry of the hydration reactions and the molar volume and weights of the C-S-A-H.

It is well established that the C/S ratio of C-S-A-H is lower in slag blended cement pastes than that in C-S-H found in Ordinary Portland Cement pastes, indicating that the slag reaction is consuming additional calcium from clinker. This additional demand is provided by the CH formed by the hydration of the Portland cement. The curing time has been found to have minor effect on the stoichiometry of C-S-A-H, contrarily to the slag proportions that modify strongly that stoichiometry. In fact, when increasing the slag over cement ratio, the C/S ratio in C-S-A-H decreases while the A/S ratio increases [64].

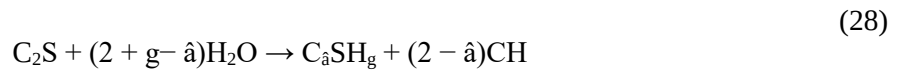
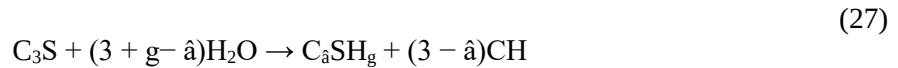
Three models are examined, depending on the different degrees of aluminum substitutions for silicone in C-S-H. These models are used to quantify the hydration products and to determine the composition of C-S-H based on stoichiometric calculations.

The three models have the following hypotheses:

- 1) **Model 1:** No CH enters the C-S-H formed by the slag hydration.
- 2) **Model 2:** CH enters C-S-H from the slag hydration to sustain a C/S ratio 1.8.
- 3) **Model 3:** Part of the CH enters C-S-H from the slag hydration (C/S varies).

Once the three models have been developed, a comparison to a series of experimental results by Richardson and Groves (1992) [69] has been carried out. In this work, only the most adequate model i.e, model 3 is retained. Model 1 and model 2 are explained in details in the works of Chen [64].

The hydration reactions of clinker phases are to be examined separately, while neglecting the hydration of minor compounds.



in which $\hat{a}$ and g are the C/S and H/S ratios in C-S-H, respectively.

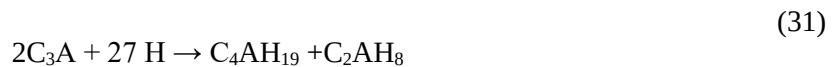
The reaction of C_3A with the presence of gypsum and water to form ettringite is:



Once the totality of gypsum in the paste is consumed by the hydration of C_3A , the ettringite begins its reaction with C_3A to form monosulfate as:



The reaction of aluminate with water can be written as:

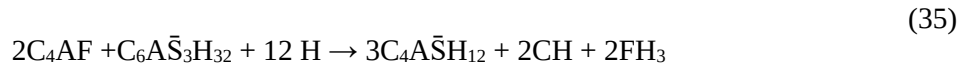
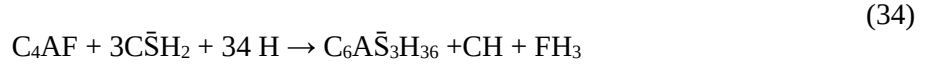




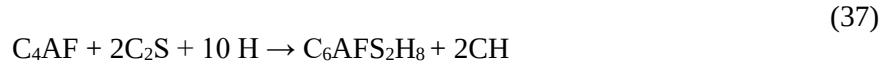
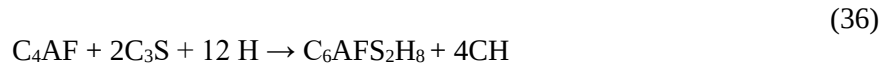
Brouwers [84] established that the C_3A reacts more likely with CH and water at room temperature to form C_4AH_{19} :



The hydration products of phases in the $C_2(A,F)$ series are comparable to those formed from C_3A with A substituted by F [76]:



The ferrite reacts with calcium silicates to form hydrogarnet in the form as [103]:



The mass and moles of the oxides for the slag are calculated in a similar way of those for the clinker while taking into consideration the fraction of the slag cement:

$$n_i^{sl} = \frac{m_i^{sl}}{M_i} = \frac{m^{sl} \times [x_i^{sl} - \sum_j x_j^{cr} \cdot x_{i,j}^{cr}]}{M_i} = \frac{m \cdot \lambda \times [x_i^{sl} - \sum_j x_j^{cr} \cdot x_{i,j}^{cr}]}{M_i} \quad (38)$$

With:

n_i^{sl} : moles of oxide i in the glass part of slag

m_i^{sl} : mass of oxide i in the glass

M_i : molar mass of oxide i

m^{sl} : mass of slag

λ : slag substitution percentage

x_i^{sl} : mass fraction of oxide i in slag

x_j^{cr} : the mass fraction of crystalline mineral j in the slag

$x_{i,j}^{cr}$: mass fraction of oxide i in the crystalline mineral j

The molar balances of major oxides in the hydration products are determined based on their respective chemical formulas, as shown in Table 6. This includes the water content associated with each hydration product at various hydration stages.

Hydration product	Formula	Quantity	Molar Balance						
			C	S	A	M	$\bar{S}$	F	H
C-S-H	$C_{\bar{a}}SA_{\bar{b}}H_g$	n_{C-S-H}	$\hat{a}$	1	$\hat{b}$				g
Hydrotalcite	M_5AH_{13}	n_{HT}			1	5			13
Hydrogarnet	$C_6AFS_2H_8$	n_{HG}	6	2	1			1	8
Ettringite	$C_6AS_3H_{32}$	n_{AFt}	6		1		3		32
Strätlingite	C_2ASH_8	n_{ST}	2	1	1				8
Tetracalcium	C_4AH_{13}	n_{AH}	4		1				13

Table 6: Molar balance of oxides in hydration products in slag blended cement.

By applying these molar balances at specific hydration degrees, the number of moles of reactants consumed during the hydration process is calculated using the formulas provided in Table 7:

Reagent	Clinker hydration	Slag hydration
C_3S	$n_{C_3S} = n_{C_3S,0} \times \alpha_{C_3S}$	—
C_3A	$n_{C_3A} = n_{C_3A,0} \times \alpha_{C_3A}$	—
C_2S	$n_{C_2S} = n_{C_2S,0} \times \alpha_{C_2S}$	—
C_4AF	$n_{C_4AF} = n_{C_4AF,0} \times \alpha_{C_4AF}$	—
gypsum	$n_{gypsum}^c = n_{gypsum,0} \times \alpha_{clinker}$	—
A	$n_A^c = n_{C_3A} + n_{C_4AF}$	$n_A^s = n_{A,0}^s \times \gamma$
C	$n_C^c = n_{C_3S} + 2 \times n_S + 3 \times n_A + n_F + n_{\bar{S}}$	$n_C^s = n_{C,0}^s \times \gamma$
F	$n_F^c = n_{C_4AF}$	$n_F^s = n_{F,0}^s \times \gamma$
M	$n_M^c = n_{M,0} \times \alpha_{clinker}$	$n_M^s = n_{M,0}^s \times \gamma$
S	$n_S^c = n_{C_2S} + n_{C_3S}$	$n_S^s = n_{S,0}^s \times \gamma$
$\bar{S}$	$n_{\bar{S}}^c = n_{gypsum}$	$n_{\bar{S}}^s = n_{\bar{S},0}^s \times \gamma$

Table 7: Consumed reagents (oxides and clinker phases) quantities.

The quantity of CH produced by the hydration of clinker and consumed by the slag hydration is calculated using the following equations:

$$n_{CH,produced\ clinker} = 1.2 \times n_{C_3S} + 0.2 \times (n_{C_2S} - 2 \times n_{C_4AF}) \quad (39)$$

$$n_{CH,consumed\ slag} = \frac{1.8 \times n_S^s - (n_c^s - 6 \times n_{AFt}^s)}{n_{CH,produced\ clinker} + (1.8 \times n_S^s - (n_c^s - 6 \times n_{AFt}^s))} \times n_{CH,produced\ clinker} \quad (40)$$

The C/S and A/S ratios in C-S-A-H are then given by:

$$C/S = \left\{ \begin{array}{l} \left(\frac{C}{S}\right)_1 = \frac{3 \times n_{C_3S} + 2 \times n_{C_2S} + n_c^s - 6 \times n_{AFt}^s - n_{CH,produced\ clinker} + n_{CH,consumed\ slag}}{n_{C_3S} + n_{C_2S} - 2 \times n_{C_4AF} + n_S^s} ; \text{ if } \left(\frac{A}{S}\right)_1 < \left(\frac{A}{S}\right)_{max} \\ \left(\frac{C}{S}\right)_2 = \frac{1.8 \times (n_{C_3S} + n_{C_2S}) + n_c^s - 6 \times n_{AFt}^s + n_{CH,consumed\ slag} + 0.85 \times n_S^s - 4 \times (n_A^s - n_{HT}^s - n_{AFt}^s)}{n_{C_3S} + n_{C_2S} - 2 \times n_{C_4AF} + 1.36 \times n_S^s} ; \text{ if } \left(\frac{A}{S}\right)_1 > \left(\frac{A}{S}\right)_{max} \end{array} \right\} \quad (41)$$

$$A/S = \min \left\{ \begin{array}{l} (A/S)_1 = n_{A^*}^s / n_S^s \\ (A/S)_{max} = \frac{1 - 0.4277 \times (C/S)_1}{4.732} \end{array} \right\} \quad (42)$$

The rationale behind these equations is further explained in [64].

The mole number of the hydration products can be then calculated using equations presented in Table 8, from that of consumed oxide in Table 7.

Products	Clinker hydration	Slag hydration
AFt	$n_{\text{gyypsum}}^c/3$	$n_S^s/3$
HT	$n_M^c/5$	$n_M^s/5$
AH	$n_{C_3A} - 2 \times n_{\text{gyypsum}}^c/3$	$\begin{cases} 0; \text{ if } (A/S)_1 < (A/S)_{\max} \\ n_A^s - n_{HT}^s - n_{AFt}^s - n_S^s \times (A/S)_{\max}; \text{ if } (A/S)_1 > (A/S)_{\max} \end{cases}$
C-S-H	$n_{C_3S} + n_{C_2S} - 2 \times n_{C_4AF}$	—
C-S-A-H	—	n_S^s
CH	$n_{CH, \text{produced clinker}}$ $- n_{CH, \text{consumed slag}} - n_{AH}^c$ $- n_{\text{monoc}}^c/2 + 2 \times n_{C_4AF}$	—
HG	n_{C_4AF}	—
monoc	$n_{\text{gyypsum}}^c/3$	—
C/S	Eq. (41)	Eq. (41)
A/S	0	Eq. (42)

Table 8: Hydration products calculation formulas.

A blended cement studied by Richardson and Groves (1992) [69] is used to be compared to the models. The oxide composition is as follows:

oxide	Clinker	Slag
C	66.5	41.15
S	20.2	36.72
A	6.2	10.86
M	1.3	7.64
$\bar{S}$	2.7	3.63
F	3.1	0

Table 9: Mass of the oxides of the cement studied by Richardson and Groves (1992) [69].

And the measured C/S and A/S for a $w/c=0.4$, 20°C :

Slag proportions	C/S	A/S
0	1.76	0.027
10	1.89	0.02
25	1.78	0.032
50	1.55	0.05
66.7	1.43	0.065
75	1.37	0.065
83.3	1.38	0.075
90	1.28	0.075
100	1.14	0.095

Table 10: The experimental results of C/S and A/S by Richardson and Groves (1992) [69].

Figure 12 and Figure 13 plot the C/S and A/S ratio in C-S-A-H versus slag proportions in cement assuming hydration degrees $\alpha=1$ for cement and $\gamma=0.7$ for slag. Chen & Brouwers' model is compared to experimental data provided by Richardson and Groves (1992) [69]:

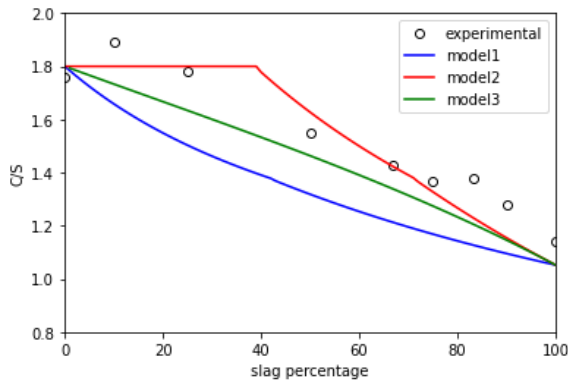


Figure 12: C/S ratio to the slag percentage.

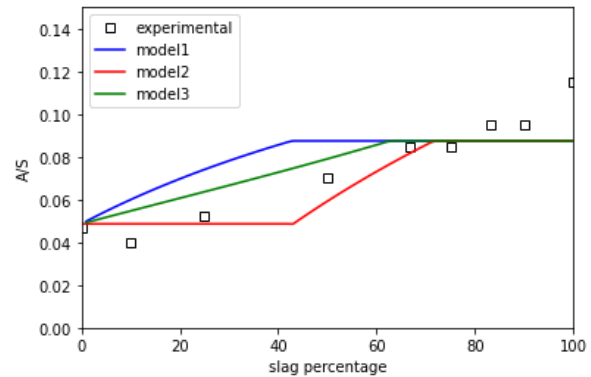


Figure 13: A/S ratio to the slag percentage.

These graphs are slightly different from the ones presented in Chen, potentially due to challenges in managing the crystalline phase (equation (38)).

Model 1 shows a C/S ratio lower than measurements and A/S ratios higher than measurements which is reasonable because this model doesn't include the intervention of CH in the slag hydration.

Model 2 shows a more correct result regarding the C/S ratio which indicates that CH from Portland cement hydration enters the C-S-H from the slag hydration. On the other hand, the A/S are slightly lower than the measurements.

Model 3 shows both C/S and A/S ratios in C-S-H close to the measurements.

These models come along with the hypothesis that the CH produced by Portland cement hydration is used by the hydration of the slag, increasing the C/S ratio and decreasing the A/C in the C-S-A-H of slag blended cement compared to the hydration of pure slag.

In this thesis, the model is also validated on other experimental data obtained from various literature sources. The corresponding compositions of these experiments are detailed in Table 11:

Cement number	Reference	Clinker oxides						Slag oxides					Mixture parameters		
		C	S	A	M	$\bar{S}$	F	C	S	A	M	$\bar{S}$	w/b	λ	T°C
Cement 2	Taylor et al. (1985) [95]	68.8	21.5	4.9	1.8	1.2	1.8	44.76	35.22	11.19	8.7	0.13	0.5	0.39	20
Cement 3	Harrison et al. (1987) [62]	66	21.3	5.6	1.2	2.7	3.2	44.56	35.74	11.06	8.62	0.02	0.5	0.4	25
Cement 4	Richardson (1997) [104]	70.8	26.9	1.9	0	0	0.4	41.64	36.95	12.55	8.01	0.85	0.4	0.5 & 0.9	25
	Shi et al. (1992) [105]	66.5	20.2	6.2	1.3	2.7	3.1						0.4	0	23
	Gollop (1992) [106]	63.6	19.8	5.8	2.8	2.3	3.4						0.3	0	20

Table 11: Composition of experimental mixtures for validating the C/S ratio.

The effect of slag hydration degree (γ) on the composition of C-S-A-H computed with model 3 is showed in Figure 14 and Figure 15 for the cements of Table 11:

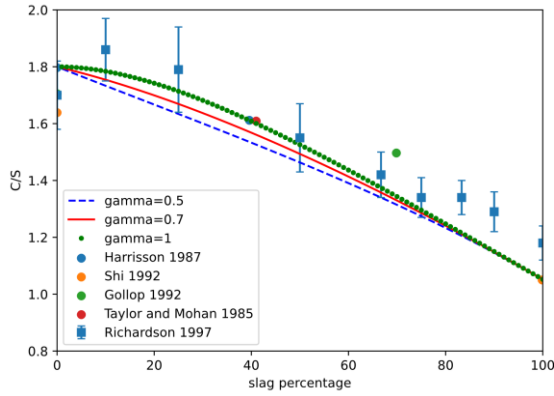


Figure 14: C/S ratio to the slag percentage.

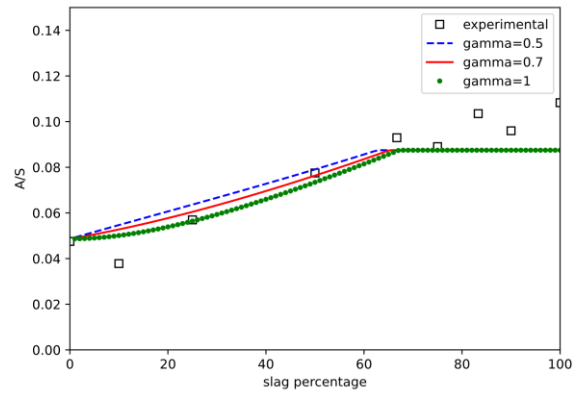


Figure 15: A/S ratio to the slag percentage.

Figure 14 and Figure 15 indicates that the results from the model align well with the experimental data. The model accurately captures the variation in C/S as the slag content increases, as the predictions closely follow observed trends, confirming its reliability.

The relationship between the S/C and A/S ratios of C-S-H is examined by using the experimental measurements. The A/S and S/C ratios in C-S-H from Cement 2, 3 and 4 are consistent with the relation proposed by Richardson ($A/C = (S/C - 0.4277)/4.732$) and employed in Chen & Brouwers' model. Figure 16 show the linearity between the A/C ratio and the S/C ratio, confirmed with multiple experiments.

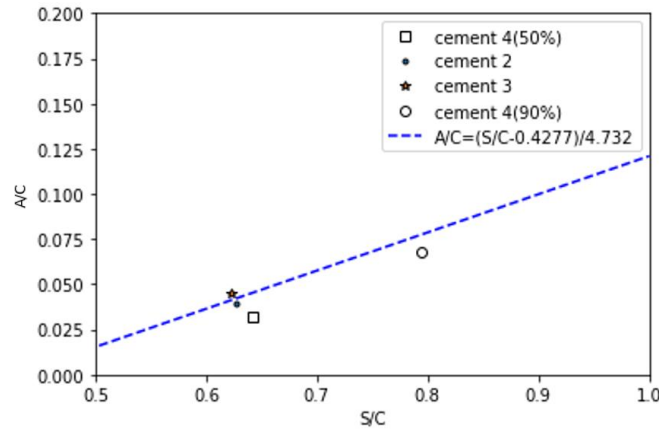


Figure 16: Linearity between A/C and S/C.

The variation in the volume fraction of the different phases as a function of slag substitution (λ), using the slag-blended hydration model, has been applied to the cement composition described by Richardson et al. [69]. The analysis is conducted for a water-to-cement ratio of 0.5, with parameters $\alpha = 1$ and $\gamma = 0.7$. The results are presented in Figure 17, illustrating the effect of slag substitution on phases evolution.

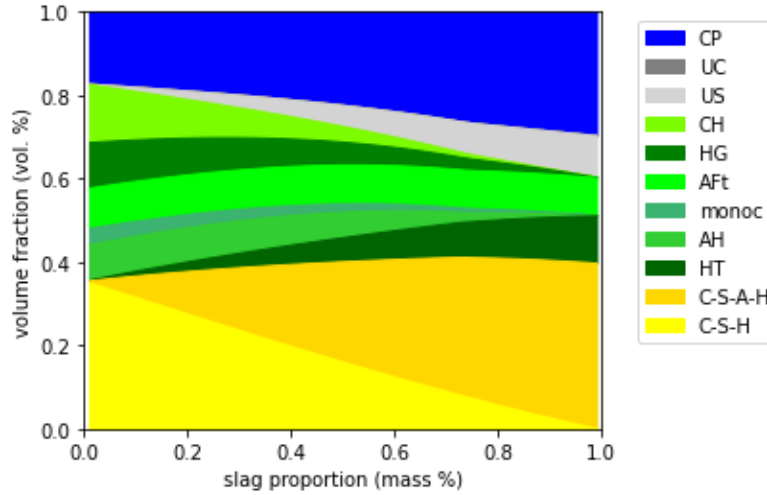


Figure 17: The variation of the cement paste phases' volume fraction depending on the slag proportion ($w/b=0.5$, $\alpha=1$, $\gamma=0.7$).

With CP being the capillary pores, UC the unhydrated clinker, US the unhydrated slag, CH the portlandite and the others as seen in Table 4. This figure presents well all the hydrates and unhydrated reactants depending on the slag proportion in cement pastes, by mass. The results given by this model do not explicitly depend on time, but on the degrees of hydration of clinker and slag.

II.2.3- Numerical models for slag blended cement hydration

II.2.3.1- Kolani's Model

Kolani [6] proposed a differential model of slag blended cement hydration based on the identification of the degrees of hydration, heat exchange, and the hydric state. A set of partial differential equations is established to govern the evolution of the corresponding variables with time. This model takes into consideration the difference in the kinetics of hydration of the slag and cement constituents, combined to a stoichiometric chemical model.

The interactions between the phases integrates a statistical approach to predict the stoichiometry of the C-S-A-H formed. The kinetics model proposed by Buffo-Lacariere [30] is adapted to take into consideration the slag blended cement hydration' specificity.

The main equations governing this model can be summed up as follows:

The rate of hydration of the anhydrous phases i in {clinker, slag} is:

$$\dot{\alpha}_i = A_i \cdot g_i \cdot \pi_i \cdot h_i \cdot s_i \quad (43)$$

where $\dot{\alpha}_i, A_i, g_i, \pi_i, h_i, s_i$ are respectively: the time derivative of the hydration degree of phase i, a global fitting parameter, the dissolution activation, the water availability, the thermal activation and the chemical activation detailed further in [12] .

The water and heat conservation equations of elementary volume within a structure is calculated by:

$$\dot{W} = -div(-D_{w0} \exp(pW) \overrightarrow{grad} W) + \sum Q_{th,i}^W \cdot f_i \cdot \dot{\alpha}_i \quad (44)$$

$$\rho c \cdot \dot{T} = -div(-\lambda \overrightarrow{grad} T) + \sum Q_{th,i}^W \cdot f_i \cdot \dot{\alpha}_i \quad (45)$$

where $W, T, D_{w0}, p, f_i, Q_{th,i}^W, Q_{th,i}^T, \lambda$ are respectively: the water content of the cement, the cement temperature, fitting parameter of the Mensi law (1998) [107], another fitting parameter of the Mensi law, anhydrous compound i mass percentage, water consumed by compound i, total hydration heat for compound i and the cement thermal conductivity.

II.2.3.2- CEMGEMS

CEMGEMS [85, 86] is a web platform that provides an easy user-interface to thermodynamic models for cementitious material hydration in the cement chemistry and engineering domain. This web app is developed and maintained in Switzerland at CONGINEER Ltd, thanks to funding from the international Nanocem consortium. The CEMGEMS web app uses the developed up-to-date GEMS3K code [108, 109] to compute chemical speciation by Gibbs energy minimization (GEM) according to the standard thermodynamic data from the Cemdata18 (Empa) and PSI/Nagra chemical thermodynamic databases[110].

CEMGEMS is used to compute the hydration process, the interstitial pore solution, the heat exchange and much more using a simple, intuitive user interface with changeable input parameters offering the results under plot views and data tables formats.

As an example, the volume fraction variation of different slag blended cement constituents depending on the hydration degree provided by the CemGEMS model is provided in Figure 18:

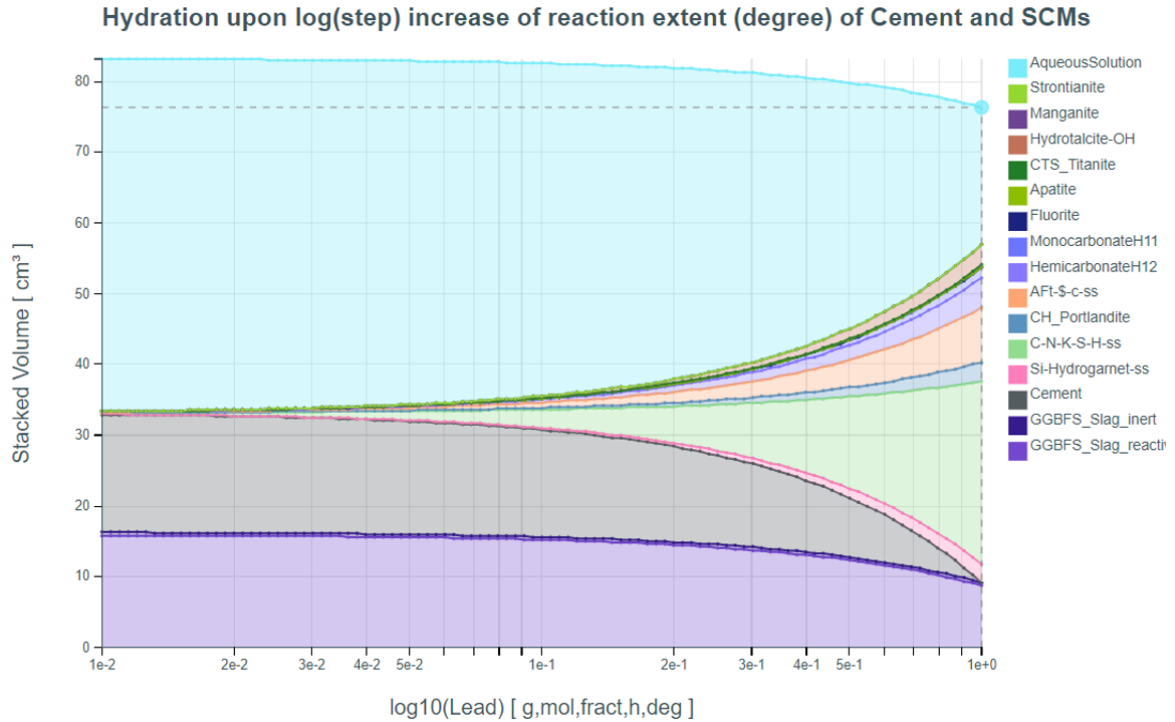


Figure 18: CEMGEMS output example ($w/b=0.4$, $\lambda=0.5$).

II.2.3.3- VCCTL

The Virtual cement and concrete testing laboratory (VCCTL) [80] is a virtual laboratory software where cement paste and concrete materials are computed in a virtual environment. It has been researched and developed for over 30 years [111–114]. The aim of this computational cement and concrete hydration modeling is to create an efficient virtual prototyping tool that quickly analyzes various concrete design combinations [115]. A solution like this might drastically minimize the amount of time and effort required to experimentally determine concrete mixes characteristics for industrial purposes.

It operates on any random mixture of cement powders, fillers, aggregates or any other cementitious material under a wide range of curing conditions. Transport properties, alongside with thermal and mechanical properties are determined over the course of the hydration. It has a graphical user interface allowing the creation, hydration and estimation of the 3D cement material microstructure.

It is based on the CEMHYD3D system, widely used in literature and for many cement types: slag blended cement [84], limestone blended cement [116], and has many applications such as porosity depercolation repercolation [117], microstructural studies [118].

The graphical user interface and an RVE example presented in the VCCTL documentation guide [119] is presented in Figure 19 below:

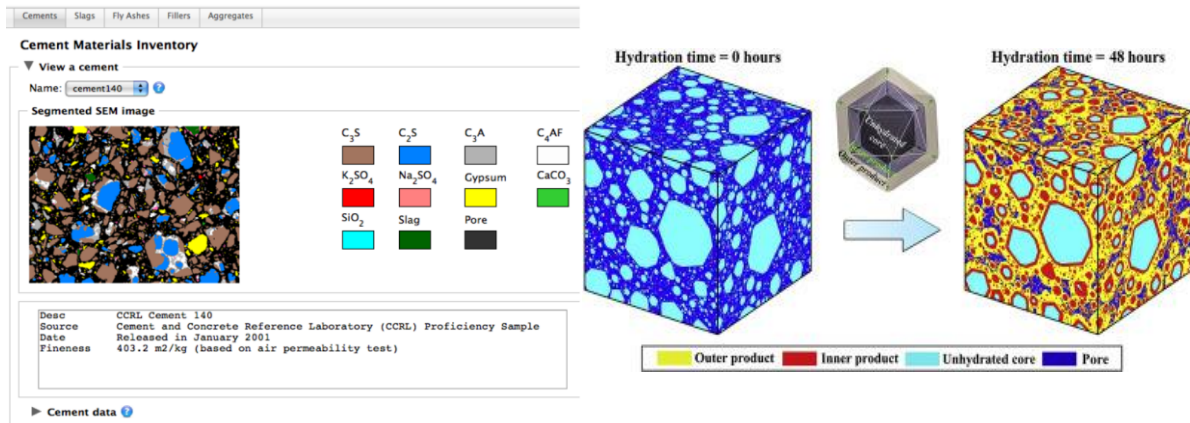


Figure 19: VCCTL: Numerical model featuring 3D voxel computations.

A representative example of VCCTL data results is shown in this graph: the volume fraction variation of different slag blended cement constituents depending on the clinker hydration degree (α):

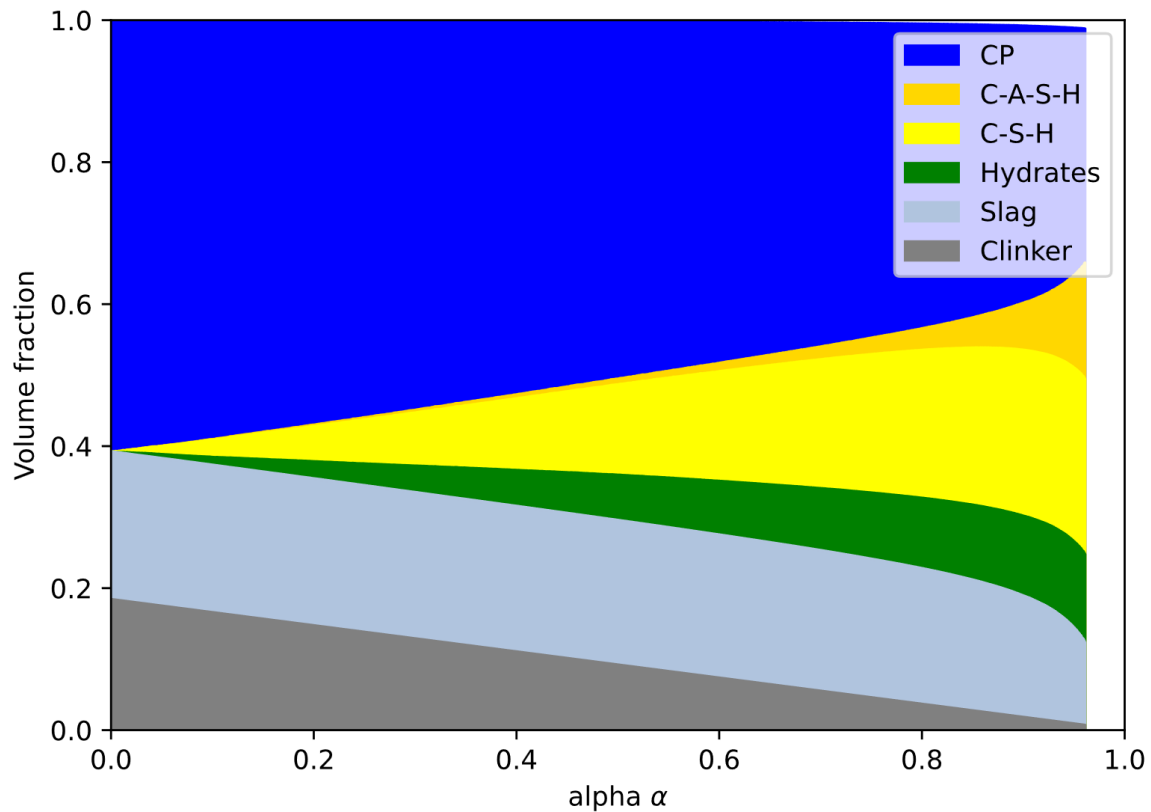


Figure 20: VCCTL output example ($w/b=0.4$, $\lambda=0.5$).

II.3- Benchmark

II.3.1- Summary of models' characteristics

A comparison between the models, regarding the input and output parameters, is provided in Table 12 below. As shown, each model presents different assets and limitations regarding the input and output parameters as well as the computational time.

Model		Powers	Tennis & Jennings	Chen & Brouwers	Kolani	CEMGEMS	VCCTL
Input	Clinker composition	×	✓	✓	✓	✓	✓
	Appropriate for slags	×	×	✓	✓	✓	✓
	Slag composition	×	×	✓	✓	✓	×
	Temperature	×	×	×	✓	✓	✓
	Curing conditions	✓	✓	✓	✓	×	✓
Output	Time dependency	×	✓	×	✓	✓	✓
	C/S of the C-S-H	×	×	✓	✓	✓	×
	Heat flux	×	×	×	✓	✓	✓
	Pore solution	×	×	×	×	✓	✓
Computational time		Instantly	Instantly	Instantly	< 1 min	Few minutes	6 hours avr.

Table 12: A summary of the assets and limitations of some slag-blended cement hydration models.

II.3.2- Comparison on the quantity of consumed and produced phases

The quantities of consumed and produced phases predicted by each selected model are compared in Figure 21. The chemical composition of binder tested in simulations is that recorded in Table 13.

Oxide	Clinker composition	Slag composition
C	63.13	42.30
S	20.68	35.90
A	4.40	11.20
F	2.34	0.30
M	2.10	8.00
$\bar{S}$	3.27	0.20

Table 13: Clinker and slag oxide composition for the cement paste used in Kolani [6].

A slag substitution rate of 50% was taken, with a water to binder ratio equal to 0.5, a clinker hydration degree of 0.98 and a slag hydration rate of 0.34. These values of hydration degrees correspond to the maximum hydration degrees simulated using VCCTL at 365 days. These binders were cured in isothermal conditions and constant temperature equal to 20°C. The results of these calculations are presented in Figure 21 below. The volume fractions' comparison of the phases regarding the porosity, the C-S-H, the C-S-A-H shows relatively close results, at the exception of hydrates formation of which VCCTL shows a large underestimation compared to the other models.

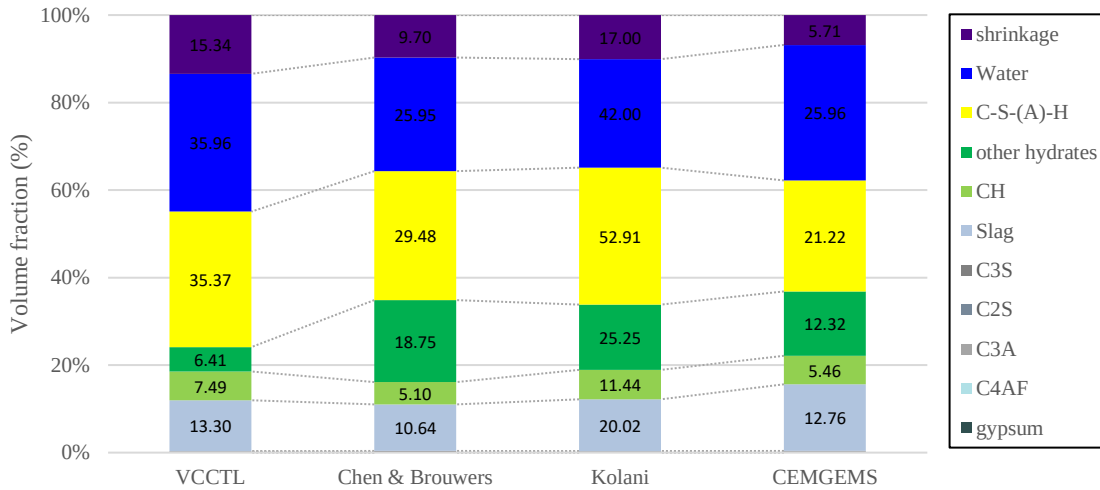


Figure 21: Phases comparison using VCCTL [80], Chen & Brouwers [51, 65, 84], Kolani [6] and CEMGEMS [85] models for a slag substitution rate of 50%, a water to binder ratio equal to 0.5, a clinker hydration degree of 0.98 and a slag hydration rate of 0.34. The key “other hydrates” denotes all hydration products not already listed in the other keys.

Another type of validation is the comparison of the mass fractions of portlandite provided by experimental campaigns carried out by Kolani [6]. For these types of comparison, experimental initial composition and conditions are taken into consideration, and the hydration rate of slag and clinker is set to be the same for all the models.

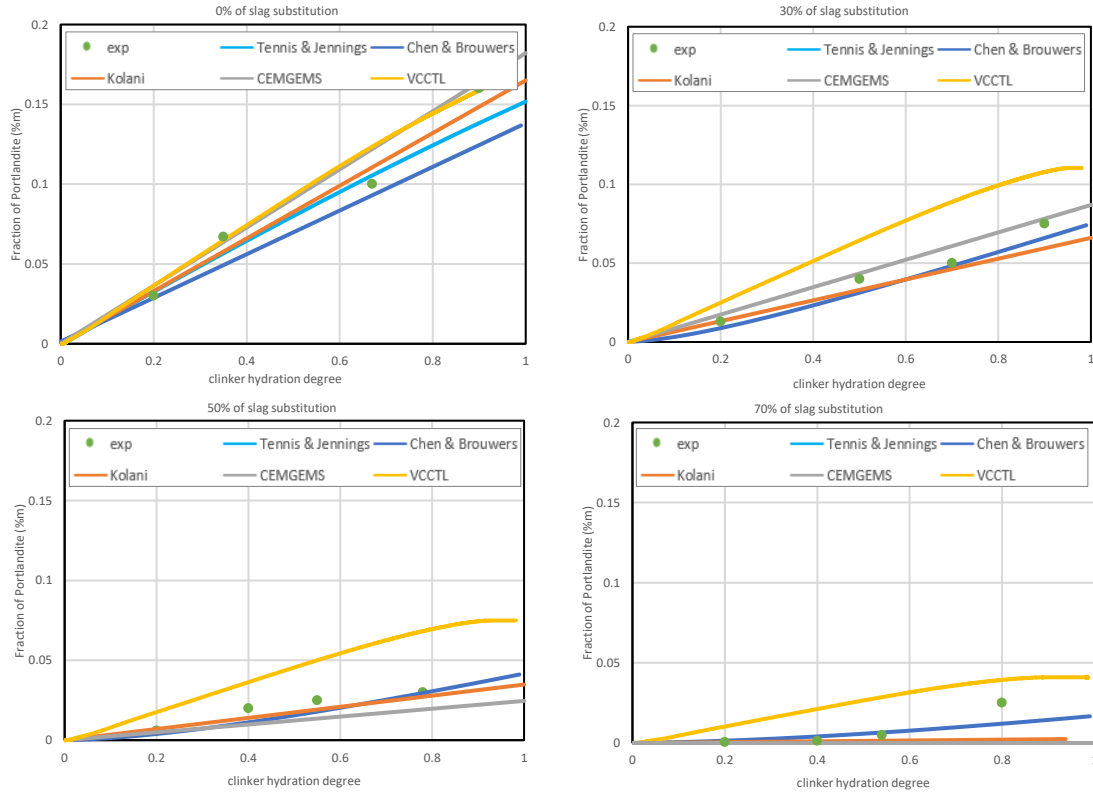


Figure 22: Comparison of experimental portlandite volume fraction measured experimentally by Kolani [6] on mixtures formulated with 0,30,50 and 70% of slag with those predicted by the selected models.

Except VCCTL that overestimates the portlandite content, the other models reproduce in a satisfactory way the experimental data provided by Kolani [6]. Gathering Figure 21 and Figure 22, it seems that VCCTL underestimates the hydration degree of slag.

The validation of others hydration products presents several issues. First, the different models do not consider exactly the same hydration products. For example, calcium monosulfoaluminate is considered as a product of slag-blended cement hydration by Kolani [6] but not by Chen & Brouwers [51, 65, 84]). Second, experimental techniques such as XRD or TGA can be interpreted differently by various authors leading to different estimation of the nature and quantities of hydration products [120].

II.4- Conclusion

A description was made of different types of models: analytical models such as Chen & Brouwers' model or Kolani's model, and numerical models such as CEMGEMS or VCCTL.

- While each type of model has its own assets and drawbacks, analytical ones seem to provide reliable results (relatively close values of porosity, portlandite, C-S-H, C-S-A-H and other hydration products) in short computational time.

- Numerical models require more computational time with outputs comparable to analytical model ones. they do however, offer valuable insights into parameters that analytical models cannot provide, such as the composition of the pore solution and pH levels.
- All these outputs models fit well to experimental data for the portlandite content, with a slight over estimation by VCCTL.

In this study, the Chen & Brouwers model was selected due to its strong alignment with the research objectives. It is a computationally efficient analytical model tailored for slag-blended cements. The model predicts the evolution of hydration phases by considering the hydration degrees of both clinker and slag, using reactants such as C_3S , C_2S , C_3A , C_4AF (derived from Bogue's calculation of CEM I oxides), along with $C\bar{S}H_2$, as well as slag. This results in the formation of hydrated phases like C-S-(A)-H, HT, AH, monoc, AFt, HG, and CH.

However, while the model successfully predicts the development of hydration phases based on the degrees of hydration for both clinker and slag, it does not account for the kinetics of the hydration process over time for slag-blended cement mixtures. To address this limitation, a kinetic study of clinker and slag hydration will be conducted in Chapter III. Subsequently, a coupled approach that integrates the Chen & Brouwers model with a kinetic hydration model for both clinker and slag will be developed and validated in Chapter IV. This coupled model will offer a more complete predictive tool for understanding hydration kinetics in slag-blended cements, further used as input parameters for the multi-scale diffusion model developed in this thesis.

Chapter III

Hydration kinetics for slag blended cements

The rate of dissolution of the different slag oxides has received little attention in the literature. In experiments, it is hard to decouple the slag hydration from the total hydration. Several experimental methods provide only a total degree of hydration by thermogravimetry XRD [121, 122]. The clinker hydration rate (taken the weighted mass into consideration) is then calculated by analytical expressions or found experimentally when studying a mixture with no slag substitution. Other methods, such as selective dissolution [123–128], give directly access to the slag hydration degree.

Kinetic laws of hydration have to be defined in hydration models to be able to describe the evolution of microstructure with time. Different types of kinetic laws have been proposed in the literature. Some hydration models (Tennis and Jennings, 2000 [83], Taylor, 1987 [96]) adopted the Avrami laws, whereas Merzouki et al. [89] discuss anhydrous dissolution (linear law), hydrate development (Avrami's law), and ion transport across the hydrate layer (diffusion of ions). According to Biernacki and Richardson [129], Knudsen's law [130] is more appropriate than Avrami's [131] or Jander's [132] equations because it offers a better description, both at a young age and over longer periods.

In most models, the clinker reactions are decoupled into phase reaction degrees of C_3S , C_2S , C_3A and C_4AF . While some authors propose a direct estimation of the clinker hydration degree without differentiating among these phases, decomposing the reactions into these four specific phases allows for a more precise and relevant estimation of the clinker's hydration degree. This approach is supported by numerous studies which demonstrate its effectiveness in providing detailed insights into the hydration process [10, 83]. The hydration degree of the four clinker phases is customarily estimated based on three successive chemo-physical processes: induction, nucleation and growth and diffusion [10]. To study the hydration kinetics of slag blended cement, it is important to understand how the pure clinker hydrates. It is important to note that, the slag substitution ratio has small to no effect on the clinker hydration kinetics. Each of its phases have their own hydration period, considering that each starts independently from the other, and each possesses its own speed rate. As for the slag hydration degree, in turn, we adopt a developed model based on a modified Knudsen's equation fitted with a large data set. Full details on the corresponding mathematical expressions for both the clinker and the slag hydration models are given in sections III - and III.2-.

III.1- Clinker hydration kinetics

The hydration reaction of the cement is exothermic, therefore the monitoring of heat release can be used as a way to determine the hydration degree [133–135]. It can be measured in laboratories by using a micro calorimeter that records the rate of heat conduction needed to keep the temperature constant. A calorimetric curve for the hydration of Portland cement is presented in Figure 23:

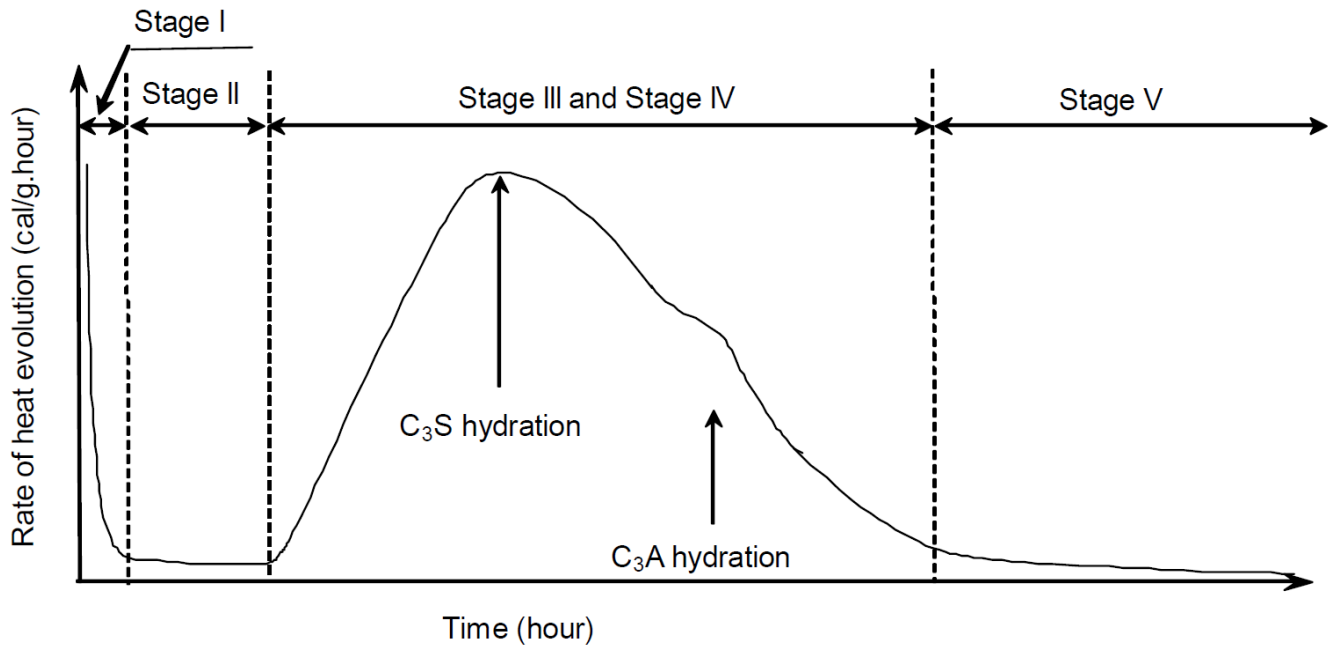


Figure 23: Schematic representation of the variation of heat release through time [136].

Five stages can be distinguished depending on different characteristics of heat release:

- Stage I: the initial hydrolysis where the dissolution of ions occurs. The dissolution of ions happens rapidly and lasts from a few minutes to 15-20 minutes after mixing.
- Stage II: the dormant stage where the ions continue their dissolution. This stage lasts for approximately 1 to 3 hours after mixing.
- Stage III: the acceleration phase where the hydration products begin to form. This phase typically lasts from 3 to 10 hours after mixing.
- Stage IV: the deceleration phase where the hydration products continue to form but slower. This phase typically lasts from 10 hours to 1-2 days after mixing.
- Stage V: the steady state where the hydration reaction occurs slowly and it can extend over several weeks to years.

In the following section, we present various analytical models that have been studied and benchmarked to understand their effectiveness and applicability in predicting and analyzing the clinker kinetics. This comparative analysis aims to highlight the strengths and limitations of each model, offering insights into their utility for specific scenarios.

III.1.1- Bernard et al. cement hydration kinetics model

Bernard et al. [10] adapted the physical chemistry model proposed by Atkins [137] to describe the kinetics of hydration of the clinker phases by nucleation and growth kinetic laws. These laws link the reaction rate

$d\alpha_i/dt$ to the respective driving force of the chemical reaction, the scaled affinity ($\tilde{A}(\alpha_i)$). These kinetic laws can be expressed in the following dimensionless form:

$$\tau_i \frac{d\alpha_i}{dt} = \tilde{A}(\alpha_i) \quad (46)$$

where τ_i is the characteristic time associated with the reaction. The characteristic time is temperature dependent describing thermal activation of the hydration reaction. This dependence is modeled by the Arrhenius concept:

$$\tau_i(T) = \tau_i(T_0) \exp \left[\frac{E_{a,i}}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right] \quad (47)$$

Where:

- R the universal gas constant ($R=8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$),
- $E_{a,i}$ is the activation energy of the chemical reaction ($E_{a,i}/R$ is equal, respectively for C_3S , C_2S , C_3A and C_4AF , to 4500, 2500, 5500 and 4200 K [99])
- $\tau_i(T_0)$ is the characteristic time of the reaction at a reference temperature T_0 ($T_0=293 \text{ K}$).

For each clinker phase the affinity $\tilde{A}(\alpha_i)$ is modeled in three processes. The details of these processes are presented in the Table 14.

	Process	Starting time	End time	$\tilde{A}$	α_i
1	Dissolution of the clinker phase (Induction)	$t = 0$	$t_{i,0}$	$\tilde{A}=1$	$\alpha_i = \frac{t}{t_{i,0}} \times \alpha_{i0}$
2	Nucleation and growth- controlled hydration	$t_{i,0}$	t_i^*	$\tilde{A}(\alpha_i) = \frac{(1 - \delta\alpha_i)}{(-\ln(1 - \delta\alpha_i))^{\frac{1}{k_i}-1}}$	$\alpha_i = 1 + \alpha_{i0} - \exp\left(-\left(\frac{t - t_{i,0}}{k_i \times \tau_i(T)}\right)^{k_i}\right)$
3	Diffusion controlled hydration	t_i^*	—	$\tilde{A}(\alpha_i) = \frac{(1 - \alpha_i)^{\frac{2}{3}}}{(1 - \alpha_i^*)^{\frac{1}{3}} - (1 - \alpha_i)^{\frac{1}{3}}}$	$\alpha_i = 1 - \left(-\frac{\sqrt{2 \times D_i \times (t - t_i^*)}}{r_p \times \sqrt{\frac{\tau_i(T)}{\tau_i(T_0)} \times \frac{\phi_0}{\phi}}} + \sqrt[3]{1 - \alpha_i^*}\right)^3$

Table 14: The affinity $\tilde{A}(\alpha_i)$ as well as the hydration degree α_i during the three processes.

The time $t_{i,0}$ correspond to when α_i reaches $\alpha_{i,0}$ (given in Bernard et al. [10]). Time t_i^* is when α_i reaches α_i^* , taken equal to 0.6 for all phases in [10]. In this work, a modified version (named Bernard-modified for later use) with values of α_i^* equal to 0.6 for C_3S and C_3A , 0.8 for C_2S and 0.4 for C_4AF was taken to fit best the experimental results. Parameters $\tau_i(T_0)$, k_i (rate constant) and D_i (diffusion coefficient) are

dependent on the water to binder ratio, and can be found in [10]. r_p represents the average clinker grain size ($r_p = 7\mu m$, depend on clinker fineness), $\frac{\phi_0}{\phi}$ represents the ratio of the reference clinker fineness ($360 \text{ m}^2/\text{Kg}$) to the clinker fineness used in the mixture.

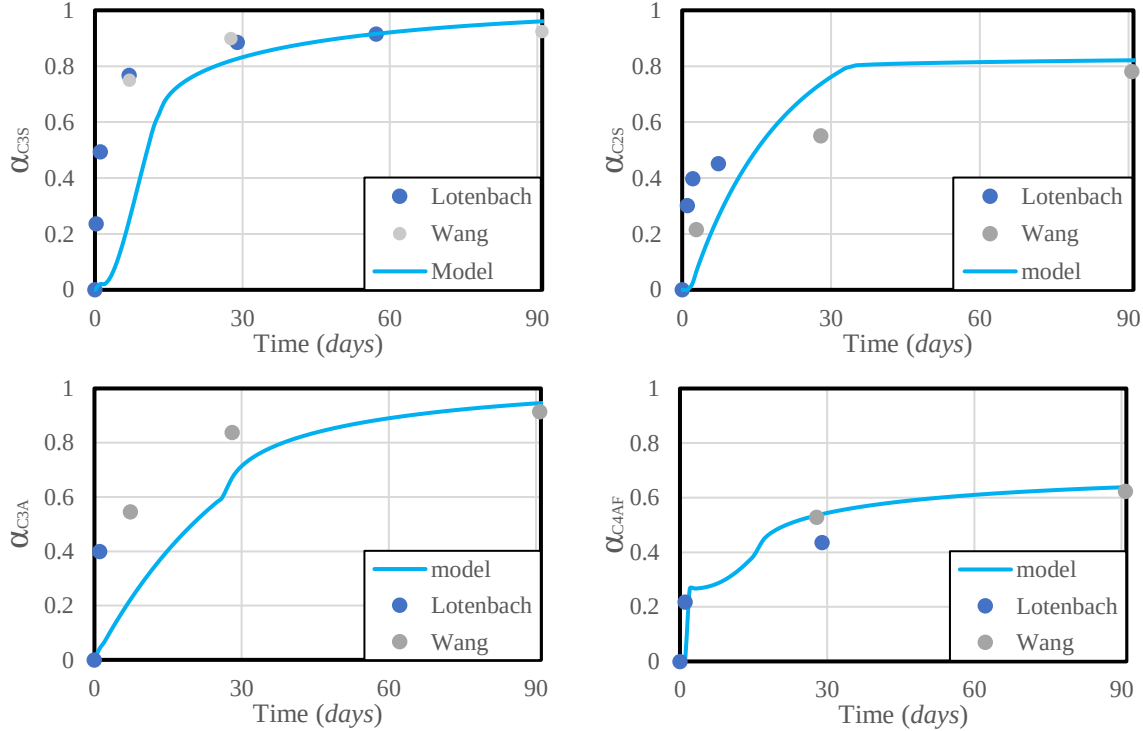


Figure 24: Evolution of the hydration kinetic for the four main clinker phases: C_3S , C_2S , C_3A and C_4AF . Experimental data by [138] and [139], model by [10].

Figure 24 validates the evolution of the degree of hydration of the four main clinker phases C_3S , C_2S , C_3A , and C_4AF for the first 90 days of hydration as a result of employing the multi-phase hydration model applied to each of the four main clinker phases and the evolution laws, with a water over cement ratio of 0.5, compared to experimental data provided by Lothenbach [138] and Wang [139] for the same water over cement ratio equal to 0.5.

III.1.2- Parrot and Killoh cement hydration kinetics model

Parrot and Killoh (PK) [140] model represents the hydration rate of individual clinker minerals in Portland cement as a function of hydration time. The hydration rate is taken as the limiting one among three hydration rates, including nucleation and growth rate, diffusion rate, and hydrate shell formation rate. The PK model allows for a relevant prediction of cement hydration under varying conditions.

The PK model calculates the hydration rates of the four main clinker phases in OPC at different ages based on empirically calibrated coefficients, which have been shown to apply to the majority of cements [141]. This model's approach is to use the slowest of the processes among nucleation/precipitation, diffusion, and reduction in transport of dissolved species at a given time to calculate the hydration rate.

One of the significant advantages of the PK model is its ability to predict the kinetics of cement hydration based on the mineralogical composition of the cement [142]. However, the model also has limitations, in particular it does not account for the water-to-cement (w/c) ratio parameter. The w/c ratio is a critical factor in cement hydration kinetics, as it influences the availability of water for the hydration reactions and the porosity of the resulting cement paste. The absence of this parameter in the PK model means that adjustments or supplementary models are often required to account for the effects of varying w/c ratios on hydration kinetics [143].

The PK model focuses on the four main clinker phases found in Ordinary Portland Cement (OPC): alite (C_3S), belite (C_2S), aluminate (C_3A), and ferrite (C_4AF). Each of these phases hydrates at different rates, contributing to the complex process of cement hydration. The analytical formulas used in the PK model to predict the dissolution rates of these phases are as follows:

1. Nucleation and growth rate (R_1): This rate is determined by the Avrami formula:

$$R_{1,i} = \frac{K_{1,i}}{n_{1,i}} (1 - \alpha_i) (-\ln(1 - \alpha_i))^{1-n_{1,i}} \quad (48)$$

where $K_{1,i}$ and $n_{1,i}$ are constants specific to each clinker phase, and α represents the degree of hydration.

2. Diffusion rate (R_2): The diffusion rate is given by the Fuji and Kondo formula [144]:

$$R_{2,i} = \frac{K_{2,i}(1 - \alpha_i)^{\frac{2}{3}}}{1 - (1 - \alpha_i)^{\frac{1}{3}}} \quad (49)$$

with K_2 being a diffusion-specific constant.

3. Hydrate shell formation rate (R_3): This rate is calculated using

$$R_{3,i} = K_{3,i} * (1 - \alpha_i)^{n_{3,i}} \quad (50)$$

where K_3 and n_3 are constants related to the formation of a shell around the hydrating particles, impeding further reaction.

The value of the discussed parameters are given in Table 15.

i	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
$K_{1,i}, \text{day}^{-1}$	1.5	0.5	1.0	0.37
$n_{1,i}$	0.7	1.0	0.85	0.7
$K_{2,i}, \text{day}^{-1}$	0.05	0.006	0.04	0.015
$K_{3,i}, \text{day}^{-1}$	1.1	0.2	1.0	0.4
$n_{3,i}$	3.3	5.0	3.2	3.7

Table 15: Parameters of the PK model reported in [145].

The hydration rate $\dot{\alpha}_i$ is then equal to the minimum of R_1 , R_2 and R_3 .

An example of the PK model applied to a cement with Bogue's composition ($m_{c3s}=0.622$, $m_{c2s}=0.109$, $m_{c3a}=0.081$, $m_{c4af}=0.067$), Temperature = 20°C and Blaine fineness = 385 m²/kg is shown in Figure 25. This example illustrates the practical application of the PK model in predicting the hydration of cement rate based on its specific chemical composition and physical properties.

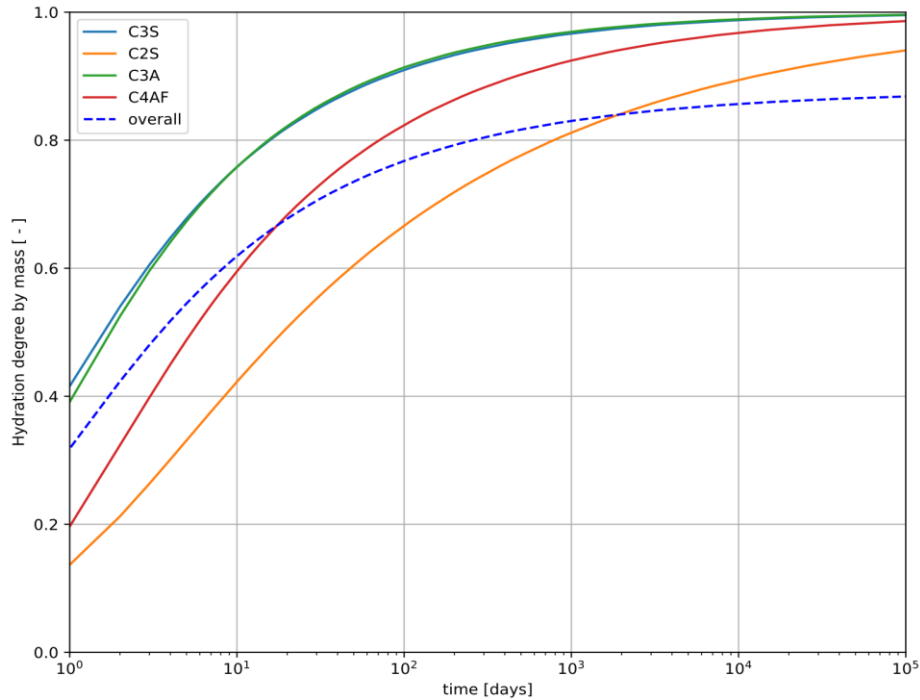


Figure 25: Results of the PK model on cement ($m_{c3s}=0.622$, $m_{c2s}=0.109$, $m_{c3a}=0.081$, $m_{c4af}=0.067$), Temperature = 20°C and Blaine fineness = 385 m²/kg.

III.1.3- Ultimate hydration degree

The total hydration degree can be calculated based on the initial phases' composition as:

$$\alpha_{total}(t) = \frac{\sum_i m_i(t) \alpha_i(t)}{\sum_i m_i(t)} \quad (51)$$

Where $i \in \{C_3S, C_2S, C_3A, C_4AF, Slag\}$ and m_i represent the mass fractions of phases i at $t=0$.

Theoretically, this total degree of hydration should be equal to 1 at the end of the hydration reactions, when time t is sufficiently big. Experimentally proven, the slag-blended cement can rarely reach its full hydration, and stops at a predefined hydration degree called an ultimate hydration degree α_u . This ultimate hydration degree is highly affected by the initial water over binder ratio W/C , the curing temperature, and the volume average of the Blaine fineness [m^2/Kg] of the clinker and slag, denoted Φ . Lin et al. [146] proposed the empirical equation of the α_u (ultimate hydration degree that can be reached by the total hydration degree of slag blended cements) by:

$$\alpha_u = \frac{\beta_1 \times W/C}{\beta_2 + W/C} \cdot \exp[-3E - 5 \cdot (T - 293)^2 \cdot SGN(T - 293)] \quad (52)$$

Where $\beta_1 = \frac{1.0}{9.33 \left(\frac{\Phi}{100}\right)^{-2.82} + 0.38}$;

$$\beta_2 = \frac{\Phi - 220}{147.78 + 1.656(\Phi - 220)} ;$$

$$SGN(T - 293) = \begin{cases} 1, & \text{when } T \geq 293K \\ -1, & \text{when } T < 293K \end{cases}$$

The suggested equation's applicability is evaluated by experimental data provided by Mills [147] and Baroghel-Bouny [148] as presented in Figure 26.

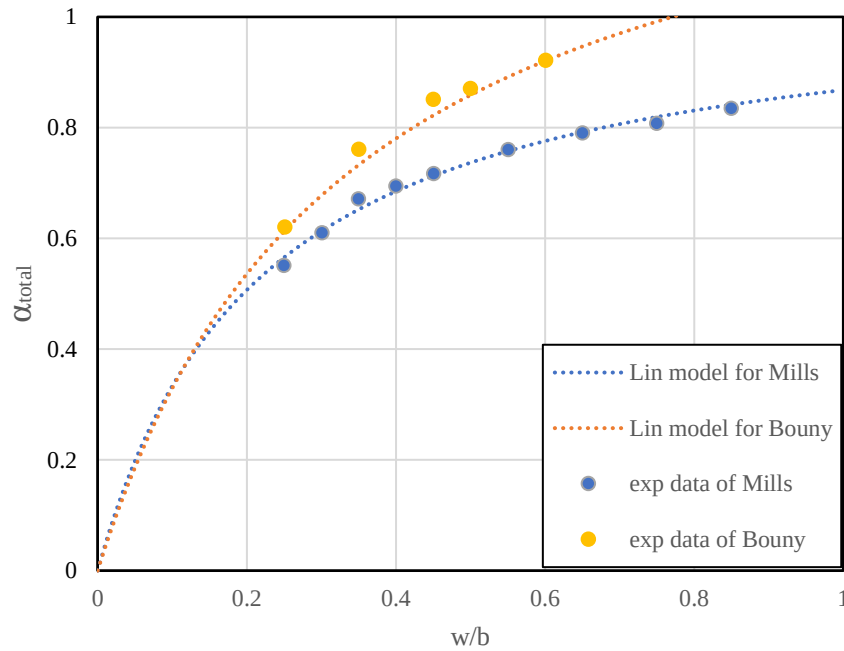


Figure 26: The ultimate degree of hydration as calculated for Mills [147] and Baroghel-Bouny [148].

III.1.4- Comparison and validation

The analytical models of clinker hydration cited previously (Bernard et al. model [10] as described in literature (Bernard-original), its variant with calibrated parameters (Bernard-modified), the Parrot and Killoh model (PK) [140] and Avrami's model (equation (26)) are compared to each other. Experimental data from Lothenbach [149] and Wang [139] with a water over cement ratio of 0.5 were used in assessing the models' accuracy for the four main clinker phases, as depicted in Figure 27. The experimental degrees of hydration for the cement mineral components of [139] and [149] were quantitatively measured utilizing Powder X-ray Diffraction/Rietveld Analysis.

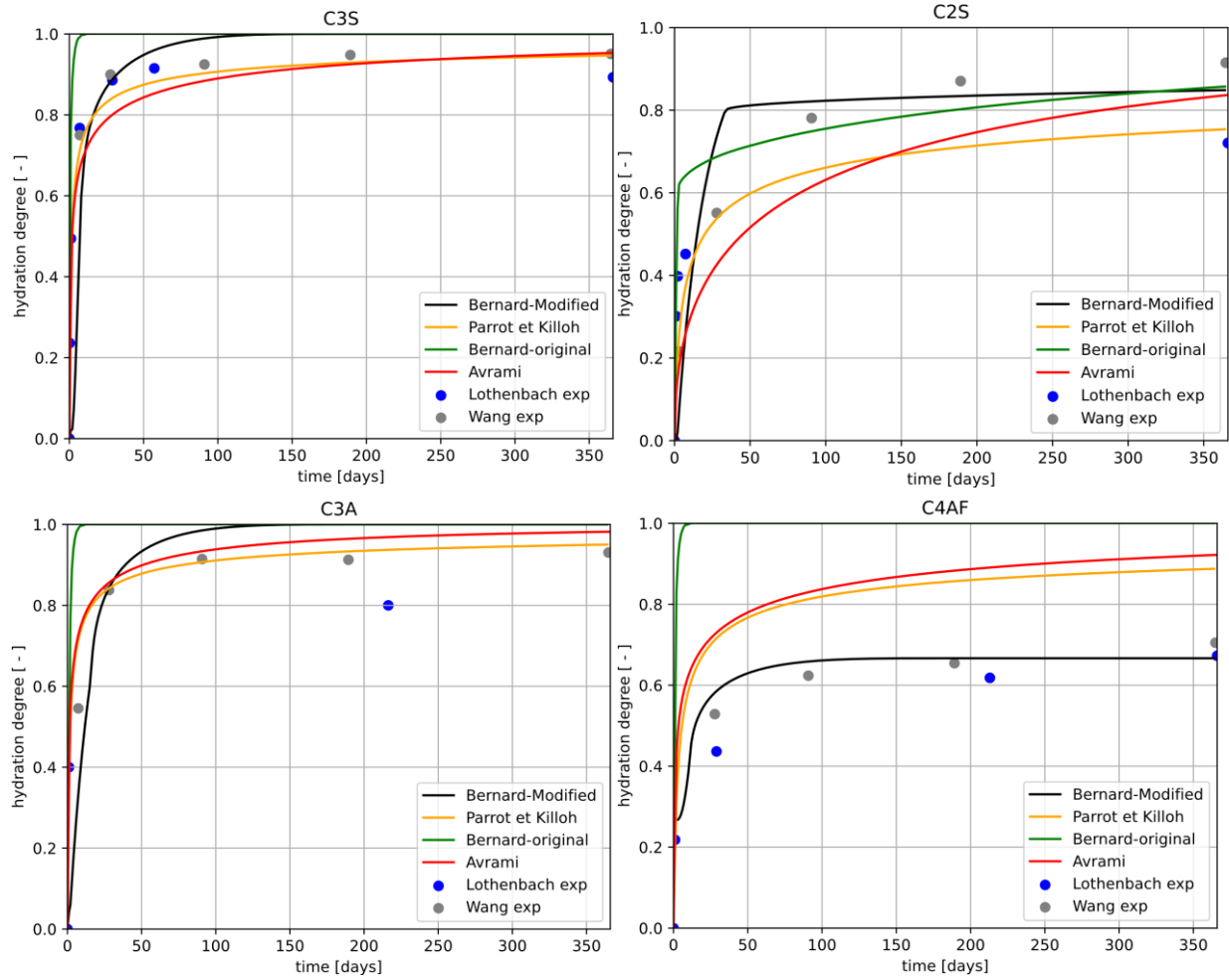


Figure 27: A comparison of hydration degree of clinker phases: model predictions and experimental results.

Initial observations indicated that the recalibrated Bernard model is suitable for the 4 main phases. Despite its effectiveness, the model does have certain limitations. It tends to overestimate the hydration progress for C_3S and C_3A after 28 days, while underestimating their hydration rates during earlier periods. Additionally, the predicted hydration curve for C_2S does not fully align with experimental data, indicating discrepancies in capturing the phase's hydration kinetics. These inconsistencies highlight areas where the model's accuracy can be further refined. The PK model exhibited valuable performance in forecasting the hydration kinetics for C_3S and C_3A , with moderately satisfactory predictions for C_2S and C_4AF .

Further validation is made on the overall hydration degree by comparing model predictions with experimental findings from Ali Ahmad [94] (for pastes with $w/b=0.5$ and no slag substitution; $m_{C_3S}=0.635$, $m_{C_2S}=0.185$, $m_{C_3A}=0.044$, $m_{C_4AF}=0.068$), derived via ThermoGravimetric Analysis (TGA). Analytical results integrate the mass proportions of the respective clinker phases, as shown in equation (6).

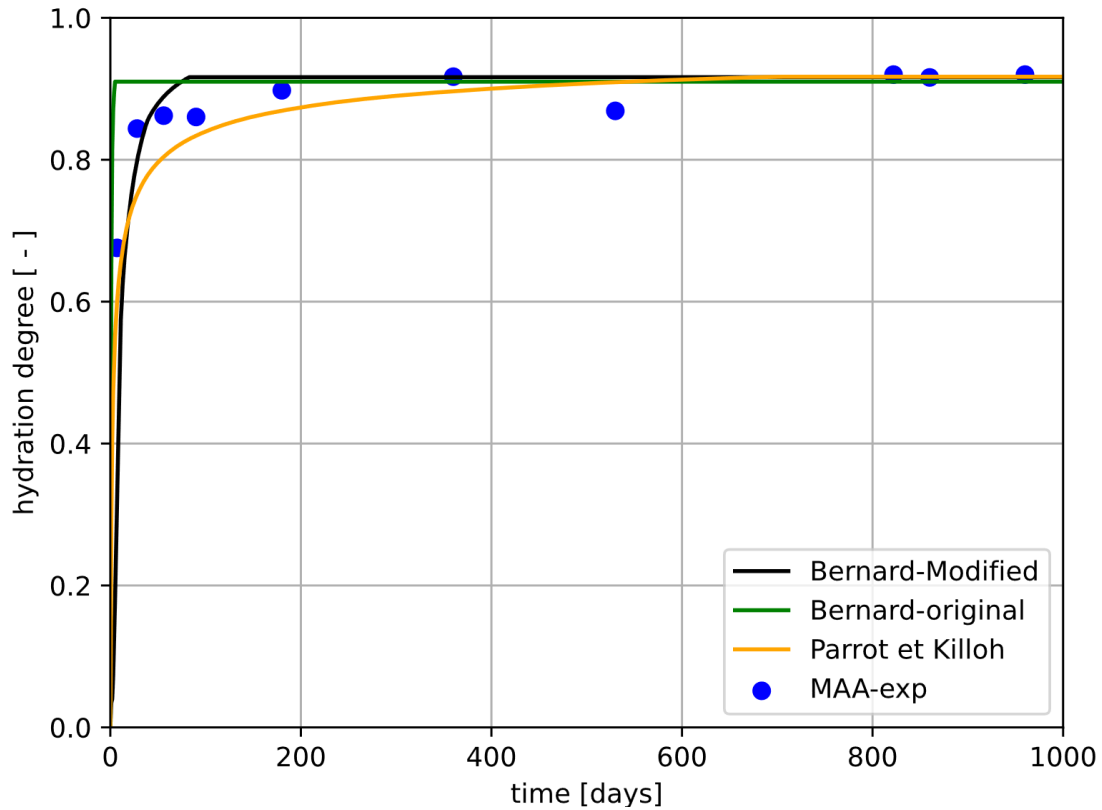


Figure 28: Total hydration degree of clinker: model predictions and experimental results.

Figure 28 reveals that both the PK and Bernard-modified models yielded trustworthy predictions, thus validating their applicability in determining the actual hydration degree of OPC paste.

However, one limitation of the PK model, as discussed in Section III.1.2-, lies in the fact that the water-to-binder ratio (w/b) is not considered as an input parameter. A comparative analysis between the Bernard-modified and PK models across varied w/b ratios (0.3, 0.5, and 0.8) is illustrated in Figure 29. It highlights that The Bernard-modified model is sensitive to changes in w/b ratios, in contrast to the PK model, which provides consistent predictions across varying w/b ratios. Given the well-documented impact of the w/b ratio on clinker hydration kinetics in literature [150–152], these findings suggest that the Bernard-modified model's is more appropriate for predicting clinker hydration kinetics. This model will be used in Chapter IV to predict the total hydration degree of slag blended cement.

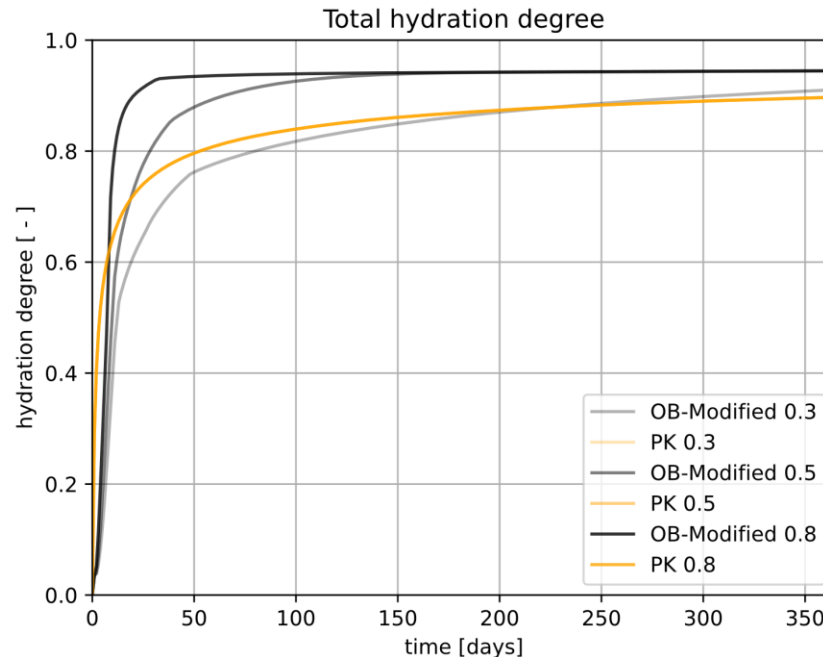


Figure 29: A comparison of the total hydration degree of clinker for different ratio of water to binder ratio.

III.2- Slag hydration kinetics

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III.2.1- Review of models and experiments on slag-blended cement and slag hydration kinetics [153]

III.2.1.1- Critical review of modeling approaches

i. Experimental methods for the determination of slag hydration degree

Currently, the most commonly used method to study the hydration kinetics of cement-based materials is the determination of the isothermal hydration heat emission curve of the material. This curve informs on the overall rate and degree of hydration of the cement and the blended mineral admixtures. Calorimetry provides valuable insights into early-age cement hydration (up to 28 days) and allows for the development of models to estimate the hydration degree evolution by analyzing heat release curves. However, it's essential to acknowledge that a model effective at early stages may not necessarily maintain accuracy over extended periods, given the slow nature of slag hydration kinetics.

Alternative experimentally-based methods for predicting hydration degree exist. They are mainly based on the ratio between chemically bound water at time t and chemically bound water for a complete hydration, *i.e.*, when t tends toward infinity. Different experimental procedures are proposed in the literature to estimate the amount of non-evaporable water at time t : from Loss On Ignition (LOI) measurements between 105°C and 550°C [154] or from the interpretation of the endothermic peaks on the

differential thermogravimetric analysis results as suggested by different authors [94, 155, 156]. The amount of chemically bound water for a complete hydration ($t=\infty$) can be estimated from analytical equations [134, 155, 156] but could also be determined from geochemical modeling according to [88]. It is worth noting that the hydration degree values strongly depend on the method of determination of chemically bound water. The later may be underestimated in the case of LOI measurements due to the fact that samples are initially dried at 105°C until a constant mass is reached. As consequence, destabilization of ettringite and part of CSH phase probably occurs. Thus, hydration degrees obtained from one specific method may show discrepancies compared to those provided by another one.

The measurement of hydration degree can also be achieved using image analysis technique. A scanning electron-point counting procedure has been used by [157] to estimate the hydration degree of mineral additions such as fly ash or slag. The authors found that the results were comparable to those obtained using a selective dissolution method. Finally, Nuclear Magnetic Resonance (NMR) experiments are increasingly used to estimate the hydration degree of cementitious materials. For instance, Stephant [88] used²⁹ Si MAS NMR to determine separately the degrees of hydration of clinker and slag in slag blended cement pastes. Nevertheless, no comparison with other methods of determination of the hydration degree has been made to validate the results obtained.

In the database underpinning this study, the selective dissolution method [124] is extensively utilized by authors to quantify the hydration degree of slag-blended cementitious materials. This technique revolves around selectively dissolving the hydration products and unhydrated cement [127, 158] while leaving the anhydrous slag portion intact, based on EDTA as presented in [124]. Prior studies have disclosed multiple constraints of this method, notably concerning the partial dissolution of the hydration products [159], as well as leaving residues of certain cementitious materials and hydrated phases of slag [160, 161]. This requires the implementation of corrective adjustments to account for a margin error of $\pm 10\%$ [159]. Furthermore, Goguel [162] further proved the presence of a minor percentage of undissolved cement hydration products. Based on these observations, Demoulian [126] has refined this technique and enhanced its precision and reliability in the evaluation of slag-blended cement hydration.

ii. Models of hydration reactions in slag blended cement

Due to the coexistence of the slag and clinker hydration, the hydration reactions of slag blended cement are more complex than that of pure Portland cement [163]. This complexity is compounded by the fact that the reactions are interdependent, affecting each other's kinetics and products. Several models have been proposed to capture the interdependence of the reactions.

Chen and Brouwers [51] proposed a reaction model for slag-blended cements based on stoichiometry calculations which link the chemical compositions of the initial unreacted phases to the volumes of produced hydration products and the resulting C-S-H composition. This calculation was integrated with the hydration model developed by Van Eijk [164], enabling the prediction of the microstructure development in slag-blended cement systems. Kolani [6] introduced an incremental model that relies on

identifying the degrees of hydration, heat exchange, and hydric state and which is coupled to stoichiometric calculations for the description of chemical reactions. The model formulates a set of differential equations to govern the temporal evolution of these variables. Schindler and Folliard [165] proposed a general kinetics hydration model capable of predicting the heat release from cementitious materials. This model integrates the impacts of the cement's mineral composition, its fineness, the inclusion of supplementary cementitious materials, the ratios of mixture components, and the characteristics of the concrete. Tydlitát et al. [166] developed a hydration model for ternary blends of Portland cement, slag, and metakaolin that accounts for the interdependence of the hydration reactions of cement, slag, and metakaolin. The model can predict the evolution of hydration heat and the degree of hydration of the ternary blend at early age. They used a modified form of the Powers' model [82], which considers both the nucleation and growth of hydrates. The modified model was coupled with a diffusion-based chloride binding model to predict the chloride binding capacity of the ternary blend. The model was validated using experimental data from isothermal calorimetry and chloride binding tests. Similarly, Merzouki et al. [89] proposed a hydration model for slag cements blends that also accounts for the interdependence of the hydration reactions of cement and slag.

Recently, Ali-Ahmad et al. [94] have published a new hydration model for slag blended cements which takes both slag and clinker hydration kinetics and chemical reactions into account. The model is close to that developed by Kolani [6] with the same stoichiometric considerations for the description of chemical reactions. A simplified analytical resolution is proposed instead of the numerical one performed by Kolani, by directly defining hydration kinetic laws of clinker and slag. Moreover, the implementation of the model does not require additional experimental results such as calorimetry as input data. The input data are both material formulation and chemical compositions of clinker and slag. The model can predict the evolution with time of hydrated and anhydrous phases, of porosity and of dry density. However, the coefficients involved in the model proposed by Ali-Ahmad et al. depend only of the substitution rate of clinker by slag, and do not consider the influence of other factors such as temperature, slag fineness and proportion of reactive slag.

iii. Models of hydration kinetics in slag blended cement

The hydration kinetics of slag in blended cements is often determined by subtracting the known cement hydration degree from the total hydration of the composite material. This method assumes that the cement and slag hydrate independently, without influencing each other's kinetics. While this approach simplifies the analysis and may not accurately reflect the interactive effects present in slag blended cements, it is nonetheless conventionally widely employed whether experimentally or analytically.

De Schutter [167, 168] proposed a hydration kinetics model valid for both Portland cement and blast-furnace slag cement at early age (up to 7 days), by which the heat production rate could be deduced from calorimetry tests as a function of the actual temperature and the degree of hydration. Wang et al. [139, 169, 170] presented a hydration kinetics model at early age (up to 3 days) for composite binders containing

slag. Merzouki [89] also proposed a kinetics model for the first 6 days of hydration of a composite binder containing slag involving the chemical compositions of cement and slag, the fineness, the curing temperature, and the water-to-binder ratio. Krstulović et al. [171] proposed a hydration kinetics model for cement-based materials based on the measured data obtained by microcalorimetry for early age hydration (first 2 days). Additionally, Pane et al. [172] also studied the hydration kinetics of composite binder containing slag using differential thermal analysis, thermogravimetric analysis, and isothermal calorimetry. This model was employed to assess the hydration degree during the early stages of hydration up to 180 days. It relies on calorimetry results and necessitates experimental data to deduce the hydration degree. Wu [173] investigated the hydration kinetics of composite binder containing slag and Portland cement using an isothermal conductive calorimeter. The model's limitations lie in its stage-dependent kinetics and varying parameters, emphasizing the need for a comprehensive understanding and careful interpretation of the results.

In this comparative analysis, the selection of only two models (Chen & Brouwers [51] and Merzouki [89] more detailed below) from the literature for evaluation is based on their extensive application within the field of hydration kinetics modeling [174–176]. These models have been chosen because they represent the most prevalent and validated approaches, providing a robust benchmark against which the developed model can be assessed as shown in section III.2.1.3-.

The first retained analytical model to describe the kinetics of slag hydration in cement-based composites is the model of Chen & Brouwers [177]. The formula used to predict the slag hydration degree γ as a function of time t [days] is a modified Avrami [131] equation:

$$\gamma = [1 - \exp(-k_2(t - k_3)^{k_1})] \cdot (a^{sl}\lambda + b^{sl}) \quad (53)$$

where λ is the slag proportion, and with the calibrated parameters $k_1 = 0.46$, $k_2 = 0.12$, $k_3 = 0$, $a^{sl} = -0.36$ and $b^{sl} = 0.86$. The evolution of the degree of hydration of slag γ predicted by this model is in good agreement with experimental data used for calibration [178] for the first 365 days of hydration. A similar equation has been recently used by Ali-Ahmad [94] to describe the hydration kinetics of both clinker and slag but with coefficients values depending mainly on the slag proportion. The model's simplicity, arising from the omission of several input parameters that substantially impact hydration kinetics, potentially limits its accuracy. Additionally, the fact that it is calibrated on experimental data from a single reference may affect its applicability to situations not included in this dataset.

The second retained model is the Knudsen's model [130] adopted by Merzouki [89], and then reused by several authors such as Königsberger [66], Cui [179], Han [180], Stephant [88]. The slag hydration degree γ is calculated according to equation 2:

$$\gamma(t) = \frac{(t/\tau)^\kappa}{1 + (t/\tau)^\kappa} \quad (54)$$

where τ is the reaction characteristic time and κ is the reaction exponent. According to Merzouki [89] $\tau = ((10.4605 \times \lambda - 1.8289) \times e^{-E_a/RT})^{-1}$ and $\kappa = 1$, where λ is the slag proportion, E_a is the activation energy, R is the gas constant, and T is the absolute temperature. This model is originally calibrated for early-age hydration (up to 5 days of hydration).

To sum up, a variety of models have been developed to predict the hydration of slag-blended concrete. Each one has its own strengths and limitations. Most are calibrated on early age data from calorimetry. Further, most analytical models do not account simultaneously for all the main mixing parameters that have a significant influence on the hydration kinetics, which can limit their accuracy and applicability. Therefore, there is a need for a model that can capture these effects and provide more accurate predictions of the hydration behavior of slag-blended cements for long curing period, while remaining fast and reliable.

III.2.1.2- Construction of a database for long term slag hydration kinetics [181]

To develop our hydration kinetics formula for the long term slag hydration in blended cement composites, a comprehensive database of slag-blended cement hydration kinetics is compiled. The database is created by collecting and compiling experimental data from different references, with the aim of gathering a wide range of experimental conditions that represent different sets of parameters. This approach ensures that the resulting kinetic formula could account for the effects of a broad range of parameters on the hydration kinetics of slag-blended cement composites.

The studies of Escalante [128], Kocaba [135], Schafer [178], and Lumley [125] are selected based on their use of consistent methods for sample preparation, curing conditions, and testing procedures. All the experimental data were acquired consistently through the application of the same selective dissolution protocol based on EDTA as described by Luke and Glasser [124]. Moreover, the parameters influencing the slag hydration kinetics are well documented in these references. The collected experimental results mainly report the slag hydration degree at different time points ranging from 3 to 365 days with a few results up to 800 days.

The database covers a wide range of slag substitution rate (λ), water to binder ratio (w/b), temperature (T), slag Blaine fineness (B), hydration time (t), reactive proportion of slag ($\rho_{reactive}$) as well as of chemical composition. The latter is quantified through a mass ratio (μ) of slag C-S-A-H to slag hydrates presented as in equation (55):

$$\mu = \frac{m_{CSAH}}{m_{slagproducts}} \quad (55)$$

Where m_{CSAH} is the calculated mass of C-S-A-H produced by the hydration at α and γ equal to 1, and $m_{slagproducts}$ is the sum of all the slag hydration products: Aft, HT, AH and C-S-A-H calculated using Chen & Brouwers model detailed in section II.2.2-.

The water to binder ratio w/b ranges from 0.30 to 0.80, while the slag substitution rate ranges (λ) from 20% to 92% by weight of cement. The temperature (T) ranges from 10 °C to 50 °C, and the Blaine fineness level (B) ranges from 225 m²/kg to 561 m²/kg. The hydration time (t) ranges from 3 to 800 days and the proportion of reactive slag ($\rho_{reactive}$) from 0.53 to 1. A summary of these parameters, along with their respective minimum and maximum values, is provided in Table 16 below.

Parameters	μ	T[°C]	w/b	λ	B[m ² /kg]	$\rho_{reactive}$	Hydration time [d]
Min	0.498	10	0.3	0.2	225	0.535	3
Max	0.782	50	0.8	0.92	561	1	805

Table 16: Parameter ranges of the data collected in literature.

Table 17 shows the details of the studies [128], [135], [178, 125], included in the developed database, including the reference, water-to-binder ratio, slag substitution rate, temperature, cement fineness, and the number of degrees of hydration reported. The detailed data about the slag hydration degree for each composition subdivided over different time periods is presented in Appendix A.

Reference	Series #	Clinker						Slag						B[m²/kg] $\rho_{reactive}$		Mix and cure parameters		
		C	S	A	M	$\bar{S}$	F	C	S	A	M	$\bar{S}$	F			T[°C]	w/b	λ
Escalante [128] (used for calibration)	1	0.651	0.198	0.058	0.021	0.026	0.023	0.339	0.353	0.114	0.138	0	0.017	325*	0.97	10	0.35	0.3
	2	0.651	0.198	0.058	0.021	0.026	0.023	0.339	0.353	0.114	0.138	0	0.017	325*	0.97	30	0.35	0.3
	3	0.651	0.198	0.058	0.021	0.026	0.023	0.339	0.353	0.114	0.138	0	0.017	325*	0.97	50	0.35	0.3
	4	0.651	0.198	0.058	0.021	0.026	0.023	0.339	0.353	0.114	0.138	0	0.017	325*	0.97	30	0.5	0.3
	5	0.651	0.198	0.058	0.021	0.026	0.023	0.339	0.353	0.114	0.138	0	0.017	325*	0.97	10	0.35	0.5
	6	0.651	0.198	0.058	0.021	0.026	0.023	0.339	0.353	0.114	0.138	0	0.017	325*	0.97	30	0.35	0.5
	7	0.651	0.198	0.058	0.021	0.026	0.023	0.339	0.353	0.114	0.138	0	0.017	325*	0.97	50	0.35	0.5
	8	0.651	0.198	0.058	0.021	0.026	0.023	0.339	0.353	0.114	0.138	0	0.017	325*	0.97	10	0.5	0.3
	9	0.651	0.198	0.058	0.021	0.026	0.023	0.339	0.353	0.114	0.138	0	0.017	325*	0.97	50	0.5	0.3
	10	0.651	0.198	0.058	0.021	0.026	0.023	0.339	0.353	0.114	0.138	0	0.017	325*	0.97	10	0.5	0.5
	11	0.651	0.198	0.058	0.021	0.026	0.023	0.339	0.353	0.114	0.138	0	0.017	325*	0.97	30	0.5	0.5
	12	0.651	0.198	0.058	0.021	0.026	0.023	0.339	0.353	0.114	0.138	0	0.017	325*	0.97	50	0.5	0.5
	13	0.651	0.198	0.058	0.021	0.026	0.023	0.373	0.325	0.107	0.141	0	0.019	225*	0.535	10	0.5	0.3
	14	0.651	0.198	0.058	0.021	0.026	0.023	0.373	0.325	0.107	0.141	0	0.019	225*	0.535	30	0.5	0.3
	15	0.651	0.198	0.058	0.021	0.026	0.023	0.373	0.325	0.107	0.141	0	0.019	225*	0.535	50	0.5	0.3
	16	0.651	0.198	0.058	0.021	0.026	0.023	0.373	0.325	0.107	0.141	0	0.019	225*	0.535	10	0.5	0.5
	17	0.651	0.198	0.058	0.021	0.026	0.023	0.373	0.325	0.107	0.141	0	0.019	225*	0.535	30	0.5	0.5
	18	0.651	0.198	0.058	0.021	0.026	0.023	0.373	0.325	0.107	0.141	0	0.019	225*	0.535	50	0.5	0.5
Kocaba [135] (used for validation)	19	0.6867	0.2468	0.0211	0.0058	0.0182	0.0043	0.4159	0.3661	0.1221	0.0718	0.0063	0.0085	300*	0.995	20	0.42	0.4
	20	0.6867	0.2468	0.0211	0.0058	0.0182	0.0043	0.3248	0.346	0.1998	0.0917	0.0199	0.0047	400*	0.942	20	0.42	0.4
	21	0.6129	0.2051	0.051	0.0282	0.0278	0.0333	0.4159	0.3661	0.1221	0.0718	0.0063	0.0085	300*	0.995	20	0.42	0.4
	22	0.6129	0.2051	0.051	0.0282	0.0278	0.0333	0.3248	0.346	0.1998	0.0917	0.0199	0.0047	400*	0.942	20	0.42	0.4
	23	0.6418	0.2101	0.0463	0.0182	0.0278	0.026	0.4159	0.3661	0.1221	0.0718	0.0063	0.0085	300*	0.995	20	0.42	0.4

	24	0.6418	0.2101	0.0463	0.0182	0.0278	0.026	0.3248	0.346	0.1998	0.0917	0.0199	0.0047	400*	0.942	20	0.42	0.4
Schafer [178] (used for validation)	25	0.6583	0.2105	0.0599	0.0154	0.0088	0.0288	0.4258	0.346	0.1205	0.0028	0.0001	0.0058	349	0.95**	20	0.5	0.2
	26	0.6583	0.2105	0.0599	0.0154	0.0088	0.0288	0.4258	0.346	0.1205	0.0028	0.0001	0.0058	349	0.95**	20	0.5	0.4
	27	0.6583	0.2105	0.0599	0.0154	0.0088	0.0288	0.4258	0.346	0.1205	0.0028	0.0001	0.0058	349	0.95**	20	0.5	0.8
	28	0.6583	0.2105	0.0599	0.0154	0.0088	0.0288	0.3802	0.3037	0.161	0.1025	0.0053	0.0125	352	0.95**	20	0.5	0.4
Lumley [125] (used for calibration)	29	0.654	0.206	0.05	0.018	0.024	0.021	0.413	0.33	0.118	0.09	0.0013	0.016	498	0.81	20	0.4	0.6
	30	0.654	0.206	0.05	0.018	0.024	0.021	0.409	0.35	0.123	0.078	0.003	0.006	437	1	20	0.4	0.6
	31	0.624	0.193	0.057	0.025	0.04	0.02	0.413	0.33	0.118	0.09	0.0013	0.016	498	0.81	20	0.4	0.6
	32	0.624	0.193	0.057	0.025	0.04	0.02	0.409	0.35	0.123	0.078	0.003	0.006	437	1	20	0.4	0.6
	33	0.624	0.193	0.057	0.025	0.04	0.02	0.413	0.354	0.127	0.067	0.0014	0.003	451	0.9	20	0.4	0.6
	34	0.654	0.206	0.05	0.018	0.024	0.021	0.413	0.33	0.118	0.09	0.0013	0.016	498	0.81	20	0.4	0.5
	35	0.654	0.206	0.05	0.018	0.024	0.021	0.41	0.361	0.099	0.095	0.003	0.0079	561	0.96	20	0.4	0.5
	36	0.654	0.206	0.05	0.018	0.024	0.021	0.409	0.35	0.123	0.078	0.003	0.006	437	1	20	0.4	0.5
	37	0.654	0.206	0.05	0.018	0.024	0.021	0.413	0.354	0.127	0.067	0.0014	0.003	451	0.9	20	0.4	0.5
	38	0.636	0.198	0.058	0.028	0.023	0.034	0.413	0.33	0.118	0.09	0.0013	0.016	498	0.81	20	0.6	0.3
	39	0.636	0.198	0.058	0.028	0.023	0.034	0.413	0.354	0.127	0.067	0.0014	0.003	451	0.9	20	0.6	0.3
	40	0.649	0.199	0.064	0.012	0.029	0.022	0.404	0.336	0.134	0.083	0.0005	0.015	395	1	20	0.3	0.69
	41	0.649	0.199	0.064	0.012	0.029	0.022	0.363	0.31	0.16	0.11	0.0016	0.015	384	1	20	0.3	0.69
	42	0.649	0.199	0.064	0.012	0.029	0.022	0.4	0.368	0.112	0.077	0.0013	0.004	397	0.89	20	0.3	0.69
	43	0.654	0.206	0.05	0.018	0.024	0.021	0.413	0.33	0.118	0.09	0.0013	0.016	498	0.81	20	0.4	0.5
	44	0.654	0.206	0.05	0.018	0.024	0.021	0.413	0.33	0.118	0.09	0.0013	0.016	498	0.81	20	0.4	0.3
	45	0.654	0.206	0.05	0.018	0.024	0.021	0.413	0.33	0.118	0.09	0.0013	0.016	498	0.81	20	0.4	0.6
	46	0.654	0.206	0.05	0.018	0.024	0.021	0.413	0.354	0.127	0.067	0.0014	0.003	451	0.9	20	0.4	0.3
	47	0.654	0.206	0.05	0.018	0.024	0.021	0.413	0.354	0.127	0.067	0.0014	0.003	451	0.9	20	0.4	0.5
	48	0.654	0.206	0.05	0.018	0.024	0.021	0.413	0.354	0.127	0.067	0.0014	0.003	451	0.9	20	0.4	0.6
	49	0.654	0.206	0.05	0.018	0.024	0.021	0.409	0.35	0.123	0.078	0.003	0.006	437	1	20	0.4	0.5
	50	0.654	0.206	0.05	0.018	0.024	0.021	0.409	0.35	0.123	0.078	0.003	0.006	437	1	20	0.4	0.6
	51	0.636	0.198	0.058	0.028	0.023	0.034	0.4	0.368	0.112	0.077	0.0013	0.004	397	0.89	20	0.3	0.69
	52	0.636	0.198	0.058	0.028	0.023	0.034	0.4	0.368	0.112	0.077	0.0013	0.004	397	0.89	20	0.3	0.92
	53	0.636	0.198	0.058	0.028	0.023	0.034	0.404	0.336	0.134	0.083	0.0005	0.015	395	1	20	0.3	0.69
	54	0.636	0.198	0.058	0.028	0.023	0.034	0.404	0.336	0.134	0.083	0.0005	0.015	395	1	20	0.3	0.92
	55	0.654	0.206	0.05	0.018	0.024	0.021	0.413	0.33	0.118	0.09	0.0013	0.016	498	0.81	20	0.8	0.6
	56	0.654	0.206	0.05	0.018	0.024	0.021	0.413	0.33	0.118	0.09	0.0013	0.016	498	0.81	20	0.6	0.6
	57	0.654	0.206	0.05	0.018	0.024	0.021	0.413	0.33	0.118	0.09	0.0013	0.016	498	0.81	20	0.4	0.6
	58	0.654	0.206	0.05	0.018	0.024	0.021	0.413	0.354	0.127	0.067	0.0014	0.003	451	0.9	20	0.8	0.3
	59	0.654	0.206	0.05	0.018	0.024	0.021	0.413	0.354	0.127	0.067	0.0014	0.003	451	0.9	20	0.6	0.3
	60	0.654	0.206	0.05	0.018	0.024	0.021	0.413	0.354	0.127	0.067	0.0014	0.003	451	0.9	20	0.4	0.3
	61	0.654	0.206	0.05	0.018	0.024	0.021	0.413	0.354	0.127	0.067	0.0014	0.003	451	0.9	20	0.8	0.6
	62	0.654	0.206	0.05	0.018	0.024	0.021	0.413	0.354	0.127	0.067	0.0014	0.003	451	0.9	20	0.6	0.6
	63	0.654	0.206	0.05	0.018	0.024	0.021	0.413	0.354	0.127	0.067	0.0014	0.003	451	0.9	20	0.4	0.6

*slag fineness estimated from the grain size distribution, by comparison to values provided by Lumley [125].

**slag reactive proportion assumed to 95%, an average value for recent references.

Table 17: Material compositions and conditions of the slag hydration kinetics database. The full dataset is available in open-access at [181].

The chemical composition and full name of the oxides are found in Table 2.

III.2.1.3- Assessment of some existing hydration kinetics models against the experimental database

To highlight the importance of using a new model, a selection of existing models widely used in the literature for predicting the hydration kinetics of slag blended cement composites (Merzouki[89], Chen and Brouwers [64], VCCTL [87]) is confronted to the experimental database. The chosen models are summarized in Table 18.

In addition, we investigate a basic, Avrami's type equation:

$$\gamma(t) = 1 - \exp\left(-\left(\frac{t - t_0}{\tau}\right)^\kappa\right) \quad (56)$$

in which γ is the slag hydration degree, t is the hydration time, the parameters t_0 (induction time), τ (the reaction characteristic time) and κ (the reaction exponent) are constants independent of the influencing variables such as temperature, slag substitution, water to binder ratio and others. These parameters are adjusted by a least square method on the experimental database presented, which gives $t_0 = 3.07$ days, $\tau = 1025$ days and $\kappa = 0.281$.

Name	Reference	Model category	Equation number	Input parameters	Theoretical background	Domain used for calibration and validation
Merzouki	[89]	Analytical	(54)	T, λ	Knudsen	0 - 5 days
Chen & Brouwers	[64]	Analytical	(53)	λ	Avrami	28 - 365 days
VCCTL	[87]	Numerical	-	$T, \lambda, w/b$	CEMHYD3D	Early age and long-term

Table 18: Selection of existing slag hydration kinetics models from literature.

The predictions generated by these models were found to be significantly different from the experimental results for the same set of parameters, as shown in Figure 30. The mismatch for Merzouki's model and VCCTL is significant for high hydration degrees, which are achieved in long term hydration studies.

The coefficient of determination R^2 values obtained from the comparison were 0.44, 0.59, 0.58 and 0.40 for Merzouki, Chen and Brouwers, Avrami and VCCTL models respectively. These low R^2 values indicates that the models presented in literature are not accurate enough to capture all factors affecting slag hydration kinetics in blended cement composites for long curing period.

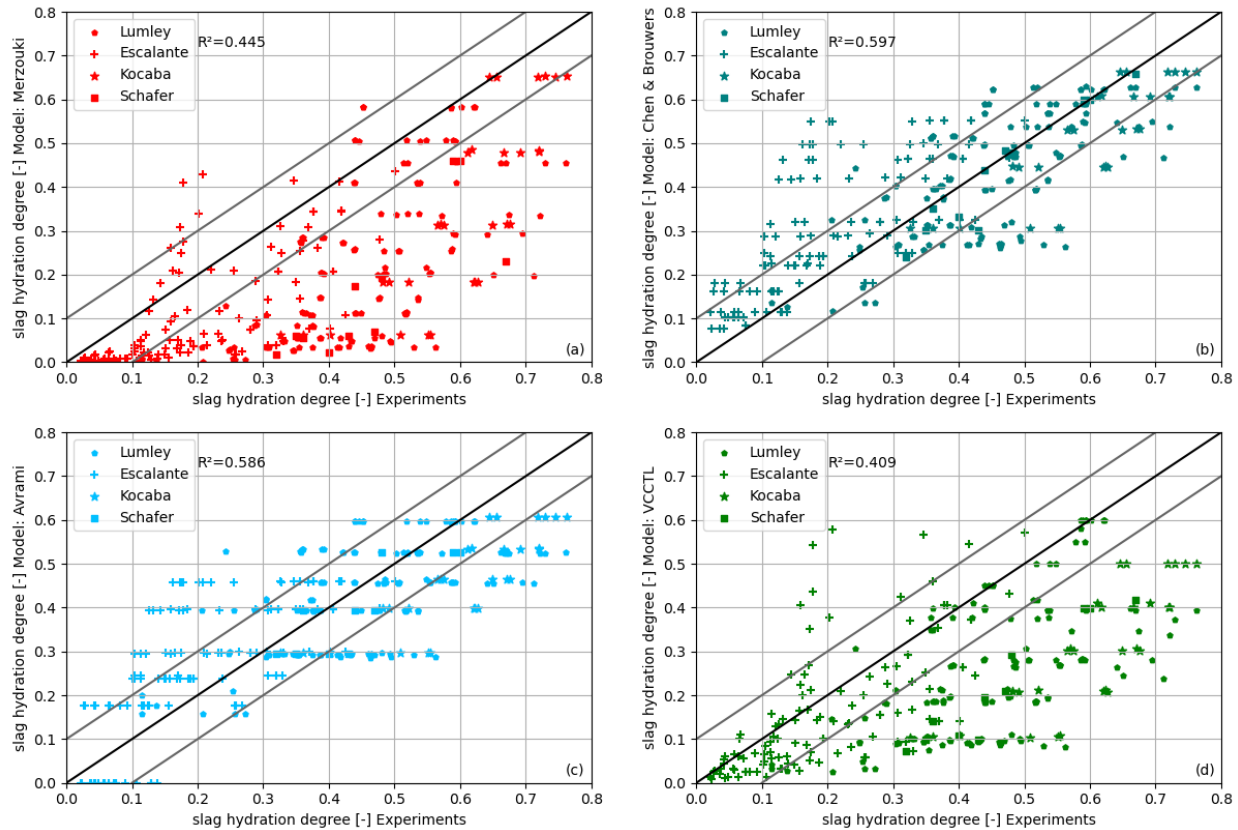


Figure 30: Comparison of different models to the experimental dataset gathered.

Upon closer examination of each model, it is observed that Merzouki's model demonstrated a notable discrepancy, indicating a significant underestimation in most cases. The VCCTL model tends to underestimate the slag hydration degree as well. Conversely, Chen & Brouwers' model exhibits a comparatively more accurate estimation, yet with a large dispersion, since it does not account for several influential parameters. Similarly, Avrami's model with constant parameters depends only on time and overlooks the other parameters that influences the slag hydration kinetics.

These results underscore the importance of developing a more comprehensive model of the slag hydration kinetics.

III.3- Modeling of slag hydration kinetics: development and validation

This section presents the development and validation of a hydration kinetics formula based on the extensive database compiled in the previous section.

III.3.1- Proposition of a new model for slag hydration kinetics

The development of a new hydration kinetics model for slag-blended cement hydration is based on Knudsen's equation, which is a commonly used equation for modeling the kinetics of phase transformation. Note that a similar methodology can be carried out on the basis of the Avrami equation

instead. Since the Avrami equation requires an additional model parameter, the induction time t_0 , we carry on with Knudsen's equation to reduce the number of model parameters.

The parameters that are taken into consideration include: the water to binder ratio (w/b), the slag substitution level (λ), the curing temperature (T), the chemical composition (through a mass ratio μ of slag C-S-A-H to slag hydrates), the proportion of reactive slag ($p_{reactive}$), and the Blaine fineness of slag (B).

To begin, it is essential to account for the influence of the slag inactive proportion during the hydration reactions. The reactive proportion $p_{reactive} \in [0; 1]$ is the mass proportion of slag that is chemically reactive. It is identified to the vitreous fraction in slag, or reactive proportion, measured using XRD. The hydration degree of slag (γ) is thus:

$$\gamma(t) = \gamma_{reactive}(t) \times p_{reactive} \quad (57)$$

where $\gamma_{reactive}(t) \in [0; 1]$ is the hydration degree of the reactive part of slag.

The kinetics of hydration of the reactive part of slag $\gamma_{reactive}(t)$ is modeled by Knudsen equation:

$$\gamma_{reactive}(t) = \frac{(t/\tau)^\kappa}{1 + (t/\tau)^\kappa} \quad (58)$$

where the reaction characteristic time τ and the reaction exponent κ are time independent functions of influencing variables. They are modeled by a separation of variables as a product of dimensionless functions C_i^τ and C_i^κ of each of the influencing variables $i \in [T, \lambda, w/b, \mu, B]$. Following a detailed assessment of different mathematical forms of functions, and their results compared to the database outlined in Table 17, the following form is retained to achieve balance between the number of model parameters and the model accuracy:

$$\tau = \tau_0 \cdot C_T^\tau \cdot C_\lambda^\tau \cdot C_{w/b}^\tau \cdot C_\mu^\tau \cdot C_B^\tau \quad (59)$$

$$\kappa = \kappa_0 \cdot C_{w/b}^\kappa \cdot C_\mu^\kappa \quad (60)$$

where the dimensionless functions C_i^τ and C_i^κ in equations (6) and (7) are defined as:

$$C_T^\tau = \exp\left(\frac{E_a}{R} \times \left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \quad (61)$$

$$C_B^\tau = (B/B_0)^{-1} \quad (62)$$

$$C_\lambda^\tau = \lambda^{a_\lambda} \quad (63)$$

$$C_{w/b}^\tau = (w/b)^{a_w} \quad C_{w/b}^\kappa = (w/b)^{b_w} \quad (64)$$

$$C_\mu^\tau = (1 - \mu)^{a_\mu} \quad C_\mu^\kappa = (1 - \mu)^{b_\mu} \quad (65)$$

where T_0 is a reference temperature set to 298 K and B_0 a reference Blaine fineness set to 450 m²/kg.

Temperature is a critical parameter in slag hydration rate, and higher temperatures lead to faster rates. Therefore, an Arrhenius-type law on the reaction characteristic time τ is adopted in equation (61) to account for temperature effects on the hydration process. In this equation, E_a represents the activation energy, R the universal gas constant (8.3145 J.mol⁻¹.K⁻¹), T the temperature in Kelvin, and T_0 the reference temperature, here 298 K.

The particle size distribution of slag particles affects the available surface area for reaction, and thus plays a significant role in the overall rate of hydration. A simple model is that the reaction characteristic time τ is inversely proportional to the specific surface area, which is expressed by equation (62) in which B_0 is a reference Blaine fineness of 450 m²/kg.

The effect of the slag substitution rate λ on the slag-blended cement hydration kinetics is modeled using a power law term on the hydration reaction characteristic time τ by equation (63). This term reflects the decrease in the rate of hydration as the substitution rate of slag increases. As more slag particles are added to the cement mixture, they replace cement particles and form a less reactive matrix.

The water-to-cement ratio is a critical parameter that influences the availability of water for the hydration reaction in slag-blended cement composites. A lower water-to-cement ratio leads to a slower hydration rate, as there is less water available for the chemical reaction to occur. This is accounted for in power law terms both on the reaction characteristic time τ and the reaction exponent κ by equation (64).

Finally, the chemical composition of the slag is also a critical parameter that affects the hydration rate. The reactivity of the slag particles depends on their chemical composition, as well as the degree to which they have reacted with the other components of the cement mixture. The chemical composition of the slag is a complex parameter that represents the different oxide compositions present in the slag. Accounting separately for each oxide proportion is cumbersome and misses chemical interactions between the oxides. To address this issue, the choice was made to express the chemical composition of the slag using a single

parameter. One effective approach is to use the ratio μ of C-S-A-H (calcium-aluminate-silicate-hydrate) formed by the slag over the total slag products that would form if all slag and clinker had reacted with water. This parameter is determined using the hydration model of Chen and Brouwers [64], as detailed in equation (55). The larger μ , the finer the porous network due to the increase in gel pores in place of capillary pores. Hence, the diffusion coefficient of ions through the hydrate layer around the hydrating slag grains is lowered, which hinders the slag reaction rate. This is accounted for by power law terms both on the reaction characteristic time τ and the reaction exponent κ by equation (65).

The values of the 8 model parameters of equations (61) to (65) are adjusted by a least square procedure on the database of Escalante [128] and Lumley [125] in Table 17. The obtained correlation coefficient is $R^2=0.805$ for the subset of the database used for calibration. Optimal values of the model parameters are provided in Table 19.

Model parameters					
E_a/R [K]	1491.9	τ_0 [days ⁻¹]	0.014	κ_0 [-]	0.077
		a_λ [-]	0.332	b_w [-]	0.635
		a_w [-]	-3.103	b_μ [-]	-1.736
		a_μ [-]	-5.839		

Table 19: Fitted values of model parameters of equations (61) to (65) on a subset of database Table 17.

We note that the fitted E_a/R value conforms with the values reported in literature [182–185].

III.3.2- Validation and illustration of the proposed slag hydration kinetics model

The model provides a more accurate representation of the slag-blended cement hydration kinetics than existing models investigated in section 2.3. We now investigate the modeled hydration rate on an independent validation subset of the database to validate the model.

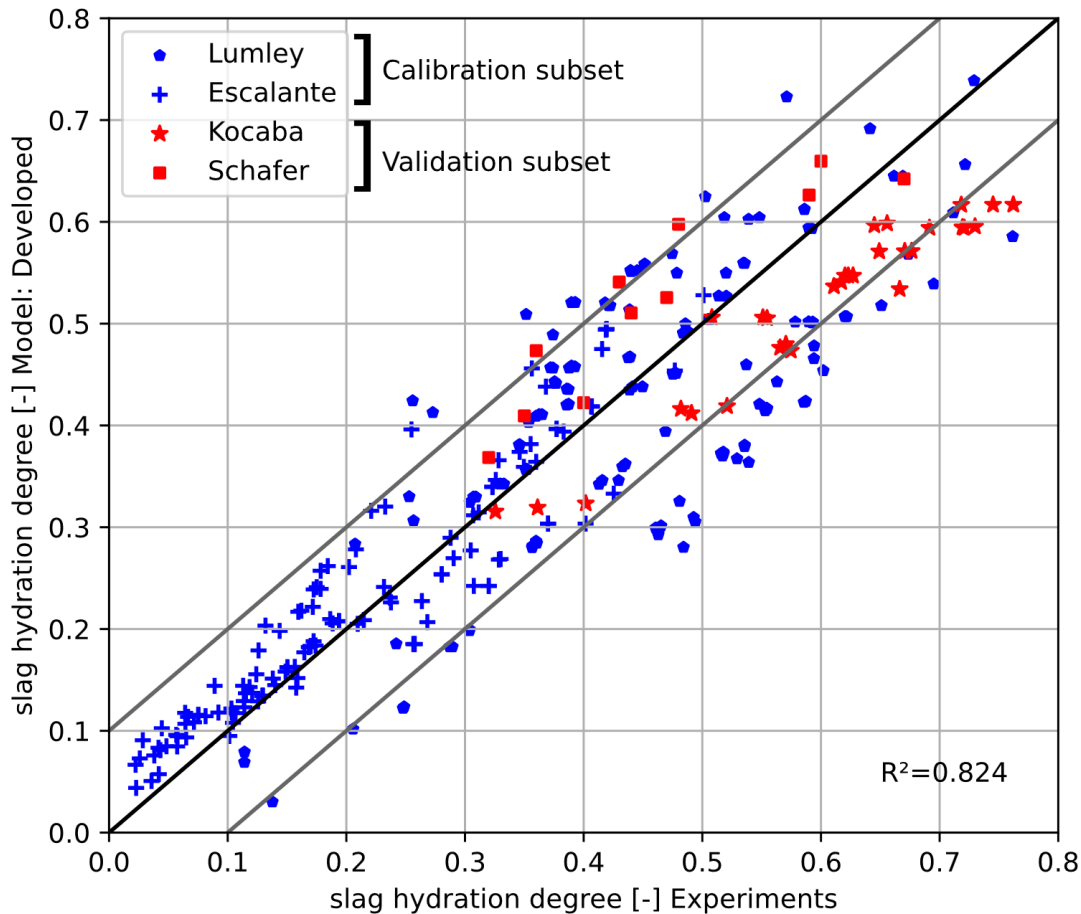


Figure 31: Validation of the developed slag hydration kinetics formula on the experimental database from Table 17.

The model parameters identified in Table 19 from the calibration subset of the database (Escalante [128] and Lumley [125]) are used on the validation subset of the database (Kocaba [135] and Schafer[178]). Results are plotted in Figure 31, with both data used in calibration (in blue) and validation (in red). Most of the points are close to the first bisector, with few results further than the $\pm 10\%$ range. The correlation coefficient for the whole database, including both calibration and validation subsets, is $R^2 = 0.824$. This correlation coefficient is larger than for the sole calibration subset. This is attributed to the fact that the data of Lumley [125] used in the calibration subset corresponds to very different configurations, while the validation subset is more homogeneous. This is further investigated below.

In Figure 32, the histogram displays the coefficient of determination (R^2) values for various models as applied to data subsets, categorized by authors. The hatched bars represent the dataset used for model fitting. The figure also includes a global R^2 value for the entire database. It is noteworthy that while alternative models may yield better results for the specific data subset of Schafer [178], the developed model is consistent with most data subsets. All models perform the worst with the data subset of Lumley [125] which covers a wide range of clinker and slag compositions.

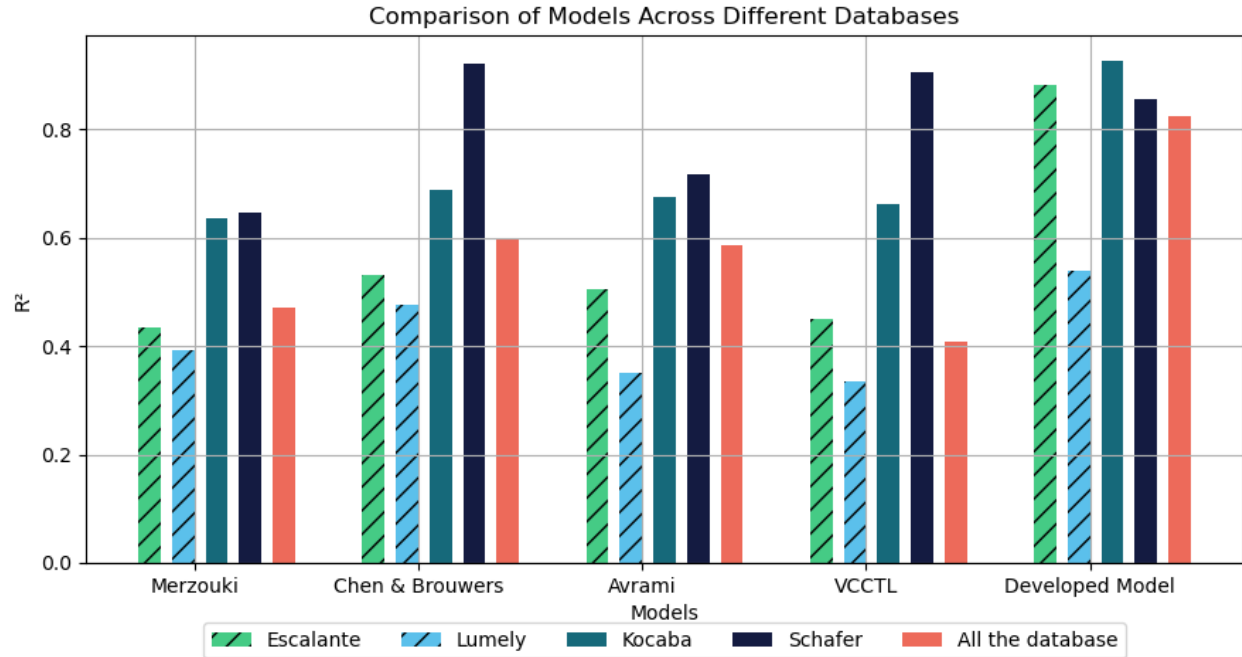


Figure 32: Comparative analysis of models' performances (R^2) across subsets of the database.

In addition, Figure 33 illustrates the evolution of slag hydration kinetics over time for the mix of Escalante [128] with $w/b = 0.5$, $\lambda = 0.5$ and $T = 10^\circ\text{C}$, 30°C , and 50°C respectively (Series #10, 11 and 12 of Table 17). These figures compare the present model with existing models and experimental data. As depicted in Figure 33, the developed model consistently demonstrates a superior fit to the experimental data across all conditions. Notably, it effectively captures the expected response of slag hydration kinetics to changes in temperature, aligning with experimental observations for long term hydration. Yet, the hydration kinetics at the lowest temperature ($T = 10^\circ\text{C}$) is overestimated at 90 and 180 days.

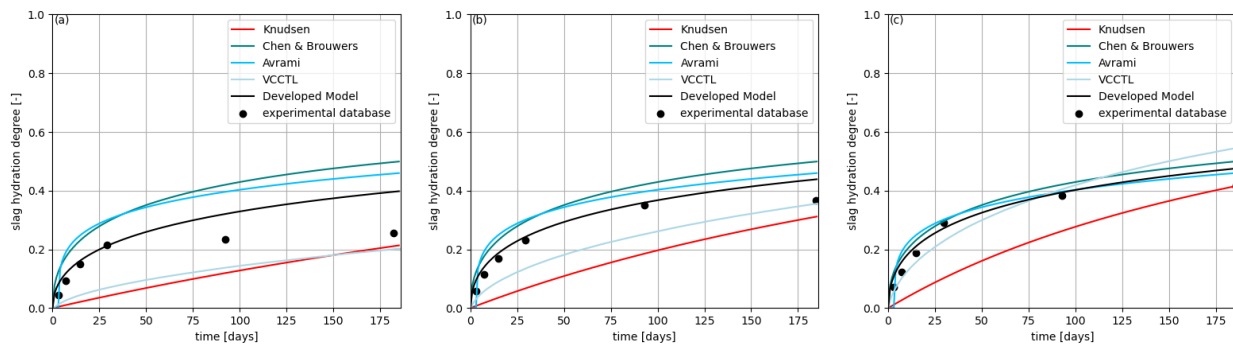


Figure 33: Models comparisons to some of the experimental results of Escalante [128] with $w/b = 0.5$, $\lambda = 0.5$ and $T = 10^\circ\text{C}$, 30°C , and 50°C respectively.

III.3.3- Sensitivity of the developed slag hydration kinetics model to variables

In order to thoroughly investigate the influence of different variables on the output of the developed slag kinetic model, a systematic analysis is conducted, incorporating a range of parameter values defined by the limits of the database (Table 17).

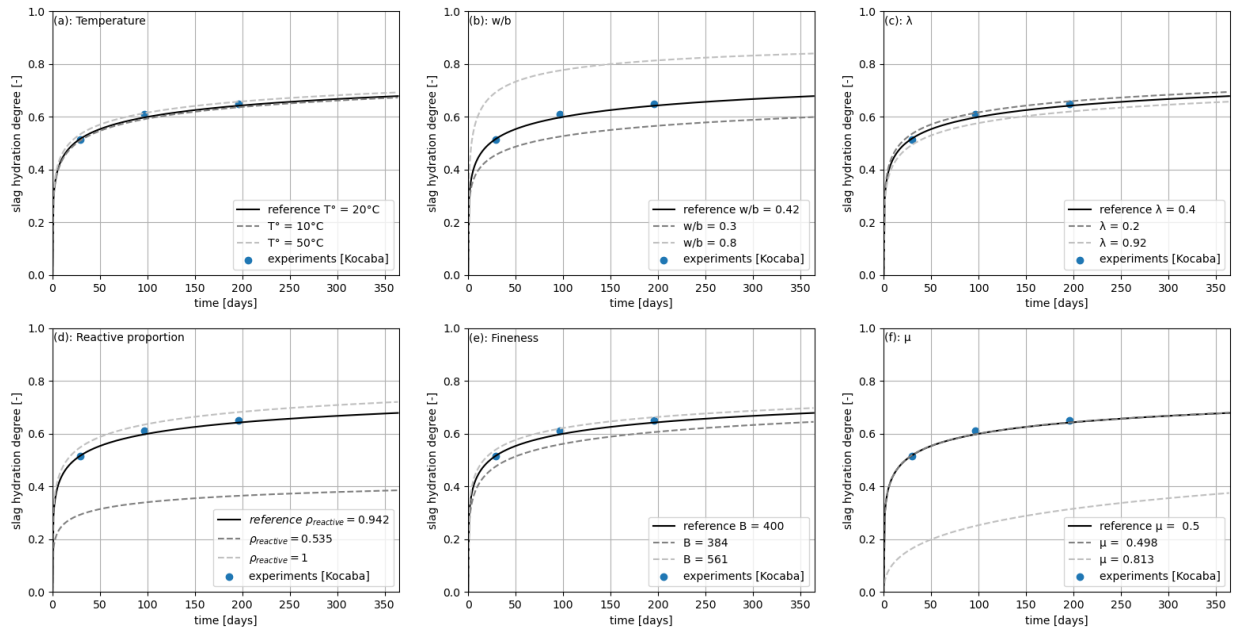


Figure 34: Influence of individual variables on slag hydration kinetics, as compared to the reference values $T_{ref} = 20\text{ }^{\circ}\text{C}$, $w/b_{ref} = 0.42$, $\lambda_{ref} = 0.4$, $B_{ref} = 400\text{ m}^2/\text{kg}$, $\mu_{ref} = 0.5$ and $p_{reactive,ref} = 0.942$ corresponding to experimental results of Kocaba [135] (#24 in Table 17).

Figure 34 provides insight on how individual variables affect the slag hydration kinetics. In each of these figures, a single variable $i \in [T, \lambda, w/b, \mu, B, p_{reactive}]$ is changed, while keeping all other variables constant. The reference variables and experimental points correspond to the formulation of Kocaba [135] with $T_{ref} = 20\text{ }^{\circ}\text{C}$, $w/b_{ref} = 0.42$, $\lambda_{ref} = 0.4$, $B_{ref} = 400\text{ m}^2/\text{kg}$, $\mu_{ref} = 0.5$ and $p_{reactive,ref} = 0.942$ (#24 from Table 17). This particular composition was chosen as most of its input parameters are close to the average parameters specified in Table 16. The hydration degree of the same experiment are plotted against three cases of the model, with only the selected variable $i \in [T, \lambda, w/b, \mu, B, p_{reactive}]$ taking the three values $[i_{min}, i_{ref}, i_{max}]$ with extreme values i_{min}, i_{max} given in Table 16. The most influencing variables are the water-to-binder ratio, the proportion of reactive slag and the chemical composition ratio.

III.3.4- Conclusion

A new slag hydration kinetics model is developed to rapidly and reliably predict the time evolution of the degree of hydration of slag in slag blended cement-based materials. The model encompasses a wide range of formulations and different experimental conditions. These conditions span variations in the chemical

composition of the clinker and slag, temperature, slag substitution ratio, water-to-binder ratio, slag fineness, and reactivity, providing a comprehensive and robust foundation for the developed model.

The proposed model is based on Knudsen equation, in which the reaction characteristic time and the reaction exponent are expressed as separate functions of influencing variables. Model parameters are identified on a first subset of the large database (239 data points) and the model is validated with the other subset (42 data points). Key findings of this study include:

- The model achieves a much better coefficient of determination R^2 than existing models frequently used in the literature.
- The slag reaction rate increases with temperature, Blaine fineness, the proportion of reactive slag, and water to binder ratio.
- The slag reaction rate decreases with higher clinker substitution by slag.
- The model takes into account a novel composite variable that encapsulates the chemical compositions of slag and clinker, enhancing the model's predictive capability. The larger this ratio μ is, the slower the reaction due to a slowdown of ionic exchange in the forming hydrate layers.

This work is a contribution towards a better quantification of the time evolution of the properties of slag-blended cementitious materials. In particular, it can be used in future together with a chemical hydration model to feed multiscale models of mechanical or transport properties based on mean field homogenization techniques.

Chapter IV

Hydration combined model of slag blended cement

This work addresses theories and an analytical model for the hydration of slag blended cement. It is based on stoichiometric relations and chemical hydration reactions for slag blended cement offered by different models, the most noteworthy in the scope of our work is the Chen & Brouwers model [64], coupled with kinetics laws that describes best the slag and clinker reactions rates. A model proposed by Bernard [10] was used to describe the hydration rates of the different clinker phases. For each of the clinker phases, this three-process multiphasic model describes an induction phase, a nucleation and growth-controlled hydration, and finally a diffusion-controlled hydration. As for the slag hydration, a developed model based on Knudsen's equation is proposed and fitted to a large data set, and then validated to prove its reliability. The results of this model are crucial inputs for the diffusion multi-scale model developed in Chapter VII.

IV.1- Combining hydration kinetics and reactions

Calculating the kinetics in paragraph III.1.1- and III.3- that provides the degree of hydration of the clinker phases and the slag as a function of time. Using them as inputs in Chen and Brouwers' model presented in II.2.2- allows a relevant approximation of the mixture composition available at any time t .

An example is given for a slag blended cement with substitution rate equal to 50%, a water to binder ratio equal to 0.5 and at a temperature equal to 25°C. The slag and cement considered are the ones used in the DEMCOM project. Their chemical characteristics are shown in Table 20.

Name	cement notation	chemical formula	Clinker composition	Slag composition
Calcium oxide, or lime	C	CaO	66.4	42.3
Silicon dioxide, or silica	S	SiO ₂	23.2	34.9
Aluminum oxide, or alumina	A	Al ₂ O ₃	3.1	10.9
Iron oxide, or rust	F	Fe ₂ O ₃	2.24	0.5
Magnesium oxide, or periclase	M	MgO	0.76	6.9
Sulfur trioxide	$\bar{S}$	SO ₃	2.22	0.1
Finesse [m ² /Kg]			363.5	445

Table 20: Oxide composition clinker and slag used for validation.

First, the different clinker phases hydration rates are calculated and presented in Figure 35 (Bernard-modified, see section III.1-). The slag hydration degree and the total hydration degree are presented in Figure 36 (Slag hydration kinetic model, see section III.2-).

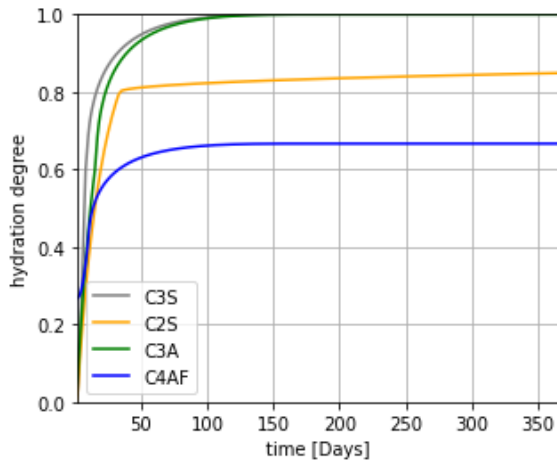


Figure 35: The hydration of the clinker phases by applying Bernard's method.

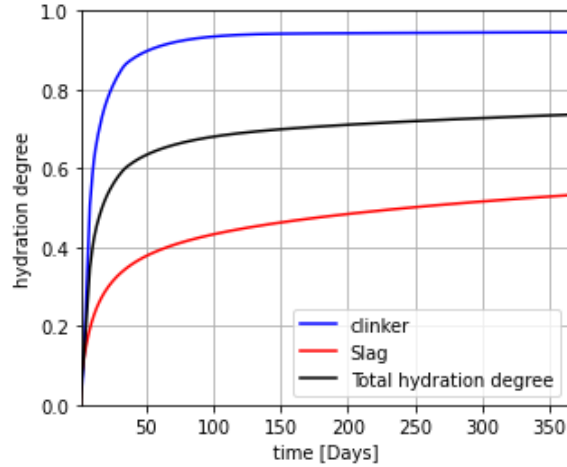


Figure 36: The hydration degree of the clinker and slag, as well as the total hydration degree.

These hydration degrees (α and γ) are input in Chen and Brouwers' model to provide the evolution of the different phases as shown in Figure 37, enabling a proper computation of the evolution of volume fractions of different components present in the slag blended cement through time.

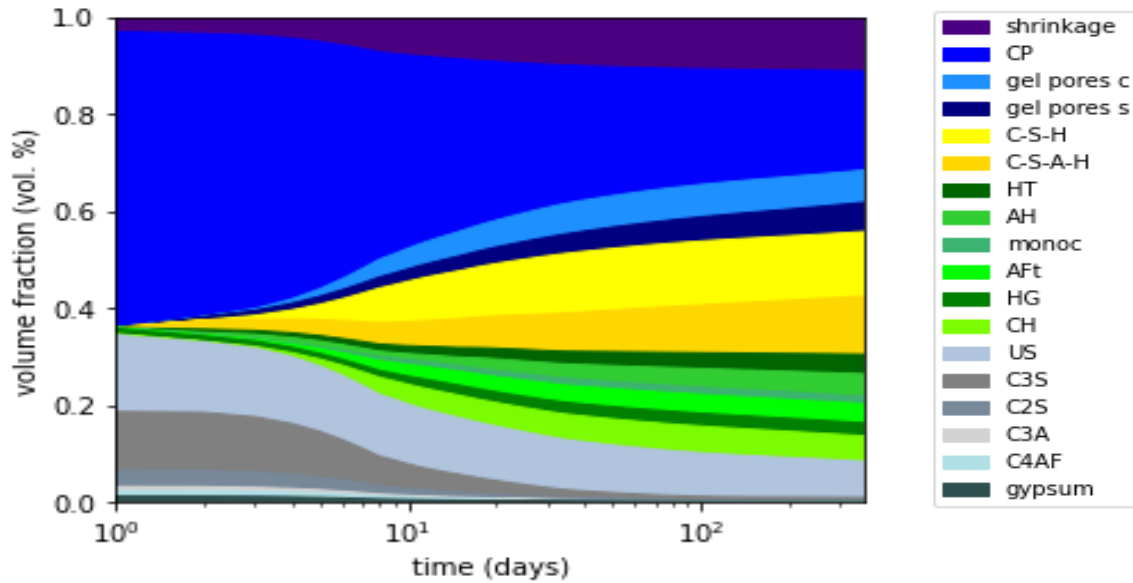


Figure 37: The evolution of the different phases with time for the DEMCOM composition (material characteristics presented in Table 20, $w/b=0.5$, $\lambda=0.5$, $T^\circ=25^\circ\text{C}$).

Figure 37 presents the outcome of this integrated modeling approach that synthesizes multiple existing models to predict the evolution of the composition of slag blended cement with time. Figure 37 illustrates the application of the combined model, showcasing how the combined models operate together to provide a detailed simulation of the material's composition evolution under specified mixture parameters.

IV.2- Various validation for the hydration model

Different validations were made, starting with the comparison of the volume fractions provided by experimental campaigns carried out by Taylor in 1985 [95] and Harrison in 1986 [62]. For these types of comparison, initial composition and curing conditions are taken into consideration, and the hydration degree of slag and clinker is identified from the residual mass of clinker and slag measured experimentally. Results for Chen & Brouwers' model show a same amount of C-S-H, a close amount of water, yet a moderate overestimation of the amounts of hydrates. The primary challenge in addressing hydration volumes lies in the divergent hypotheses regarding hydration products proposed by different researchers. The experimental data on the quantities of these hydration products are subject to varying interpretations, leading to variation among researchers. Furthermore, the analysis of the experimental XRD data, that provides the constituents of the mixture at a certain time of hydration, may be as large sources of uncertainties [120].

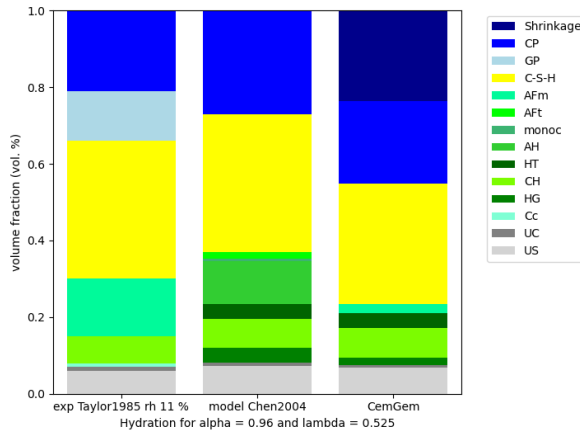


Figure 38: Chen & CemGEMS comparison with Taylor 1985's experimental results [159].

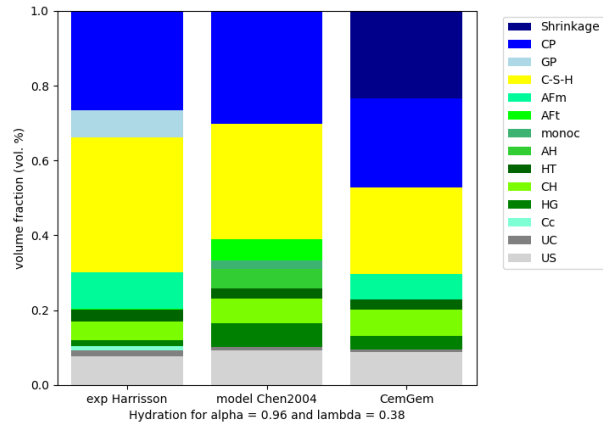


Figure 39: Chen & CemGEMS comparison with Harrison 1986's experimental results [62].

Results of Chen & Brouwers' model from Figure 37 are then compared to the numerical model VCCTL at $t=28$ days, 90 days, 180 days and 365 days in Figure 40 for the composition presented in Table 20, with slag substitution rate equal to 50%, a water to binder ratio equal to 0.5 and at a temperature equal to 25°C. The objective of this comparison is to validate the coupling of the hydration model with the kinetic models that have been proposed. The plain bars represents the results obtained by VCCTL whereas the dotted bars represents the results obtained using the presented model. It should be noted that the computational time of VCCTL's results (6 to 12 hours for each simulation) is much higher than the time needed for the presented model (almost instantaneously <1 second).

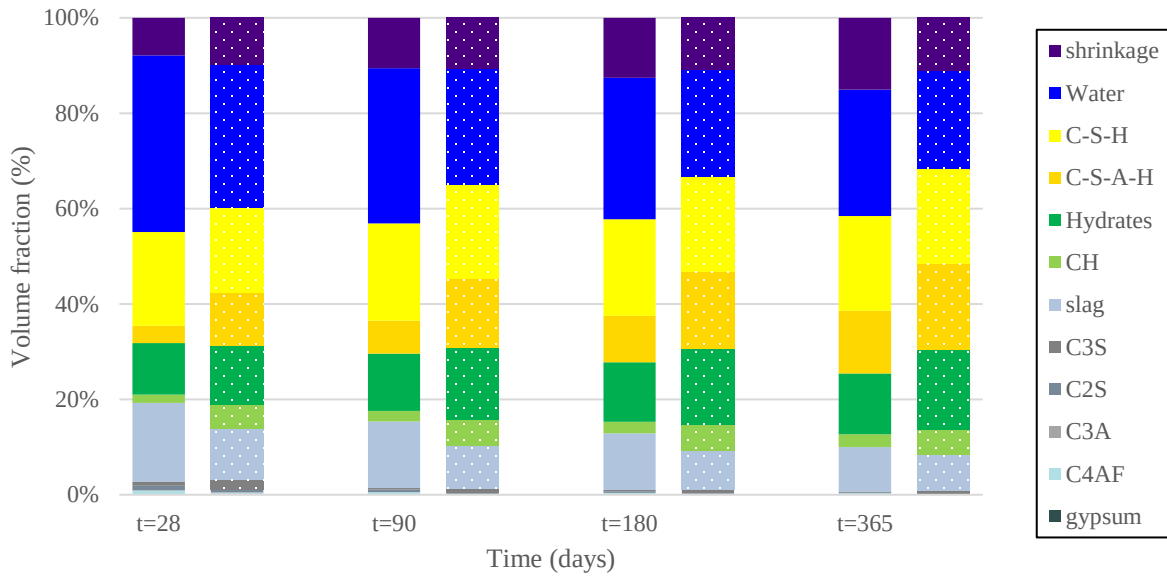


Figure 40: A comparison of the constituents' volume fraction between VCCTL (plain bars) and the developed model (dotted bar) at different time intervals equal to 28 days, 90 days, 180 days and 365 days.

Figure 40 shows a similarity in the phases' composition computed by this model and VCCTL, except for the portlandite and hydrates phases. Therefore, a more profound validation was made based on experimental results provided by Kolani [6], Iyoda and Dan [186], Li-Na Zhang [187] and Wang [139], in order to assure that the portlandite isn't overestimated.

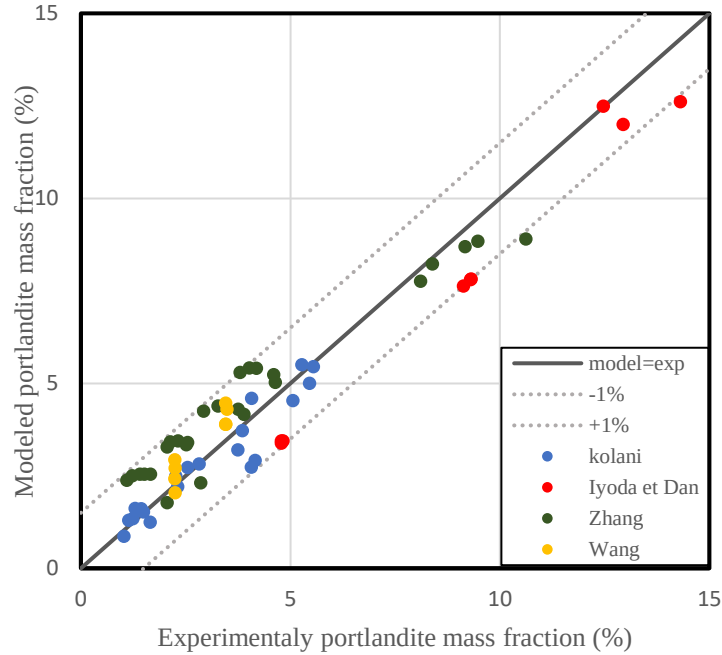


Figure 41: The validation of the portlandite mass fraction calculated with the developed model with experimental data given by [6, 139, 186, 187].

According to Figure 41, the proposed model estimation of portlandite content is close to experimental one with a margin of $\pm 1\%$.

In the following phase of the validation process, the integration of the proposed hydration model with the previously introduced kinetic models for clinker and slag hydration is assessed. This involves a detailed comparison between model computations and experimental outcomes derived from X-ray Diffraction (XRD) analyses conducted by Taylor [95, 188], which characterize the phase composition of slag-blended cement after a hydration period of 14 months for a water to binder ratio w/b of 0.5 and $\lambda=0.4$.

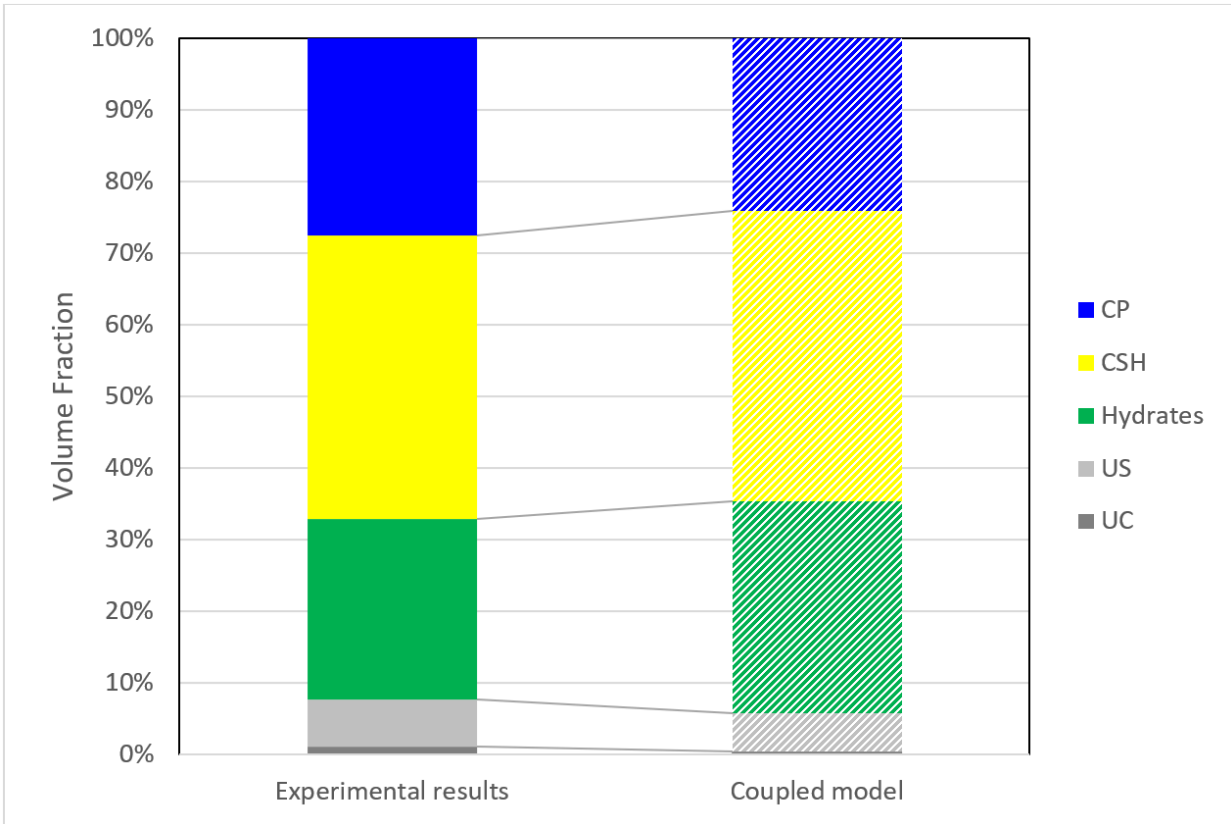


Figure 42: Comparison between the developed coupled model and experimental results by Taylor [159, 188].

The comparative results are illustrated in Figure 42, underscoring the model's accuracy against empirically obtained data, thereby substantiating the model's efficacy in simulating the hydration dynamics of slag-blended cement systems.

Another comparative analysis is presented in Figure 43 to validate the coupling technique employed between various proposed models for clinker and slag hydration and kinetics. The experimental data serving as the benchmark for this comparison originate from studies conducted by Gruyaert et al. [189], which focused on cement samples with a water-to-binder ratio (w/b) of 0.5, varying slag substitution rates ($\lambda=0, 0.482, 0.8$), and assessed at two significant hydration intervals: 28 days and 540 days. These studies utilized Backscattered Electron (BSE) imaging techniques to quantitatively assess the phase compositions within the cement matrix, providing a detailed basis for model evaluation.

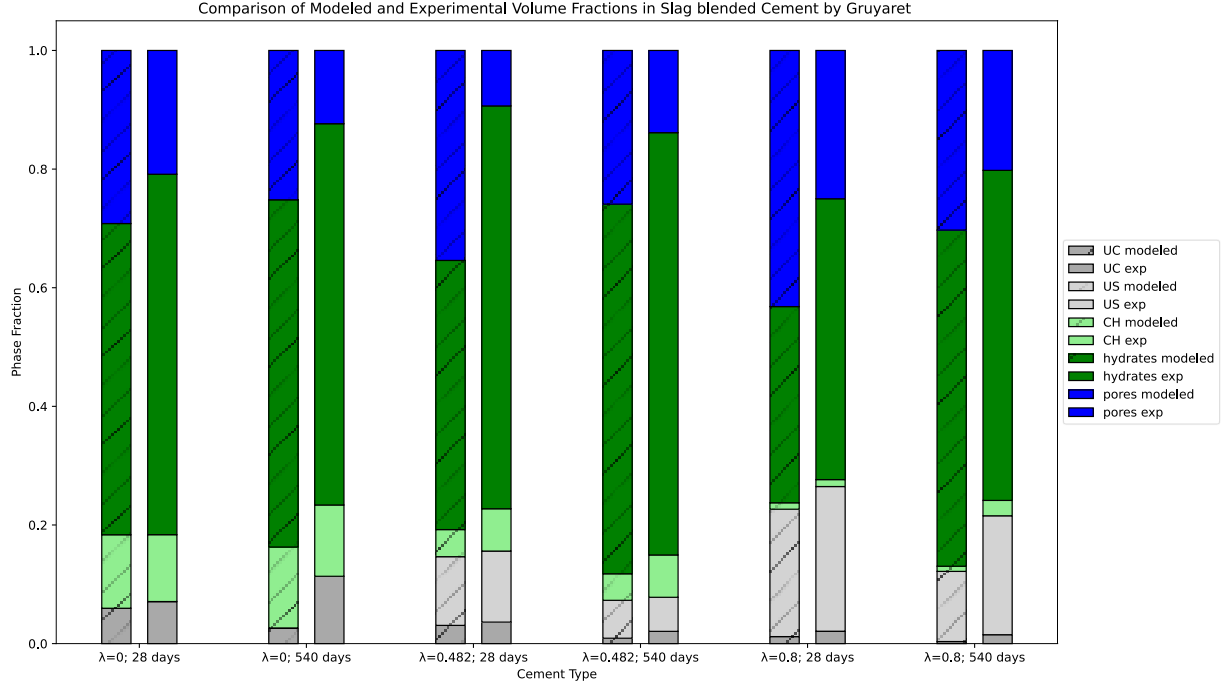


Figure 43: Comparative Analysis of Modeled and Experimental Phase Composition in Slag-Blended Cement.

Figure 43 presents a side-by-side comparison of modeled (hatched) versus experimental results (plain) across 3 categories of cementitious materials each at a hydration time of 28 or 540 days. Each category is further broken down into the constituent phases: unhydrated clinker (UC), unhydrated slag (US), calcium hydroxide (CH), hydrates, and pores, thereby offering a comprehensive view of the material composition at varying stages of hydration.

Upon analysis, the model aligns closely with the experimental data provided by Gruyaert [189]. While minor discrepancies are observable, they fall within an acceptable range, attributable either to inherent experimental variances or the limitations of predictive modeling. Such validation underscores the pertinence of the proposed combination of different models, enhancing our ability to model the complex hydration processes of cementitious materials.

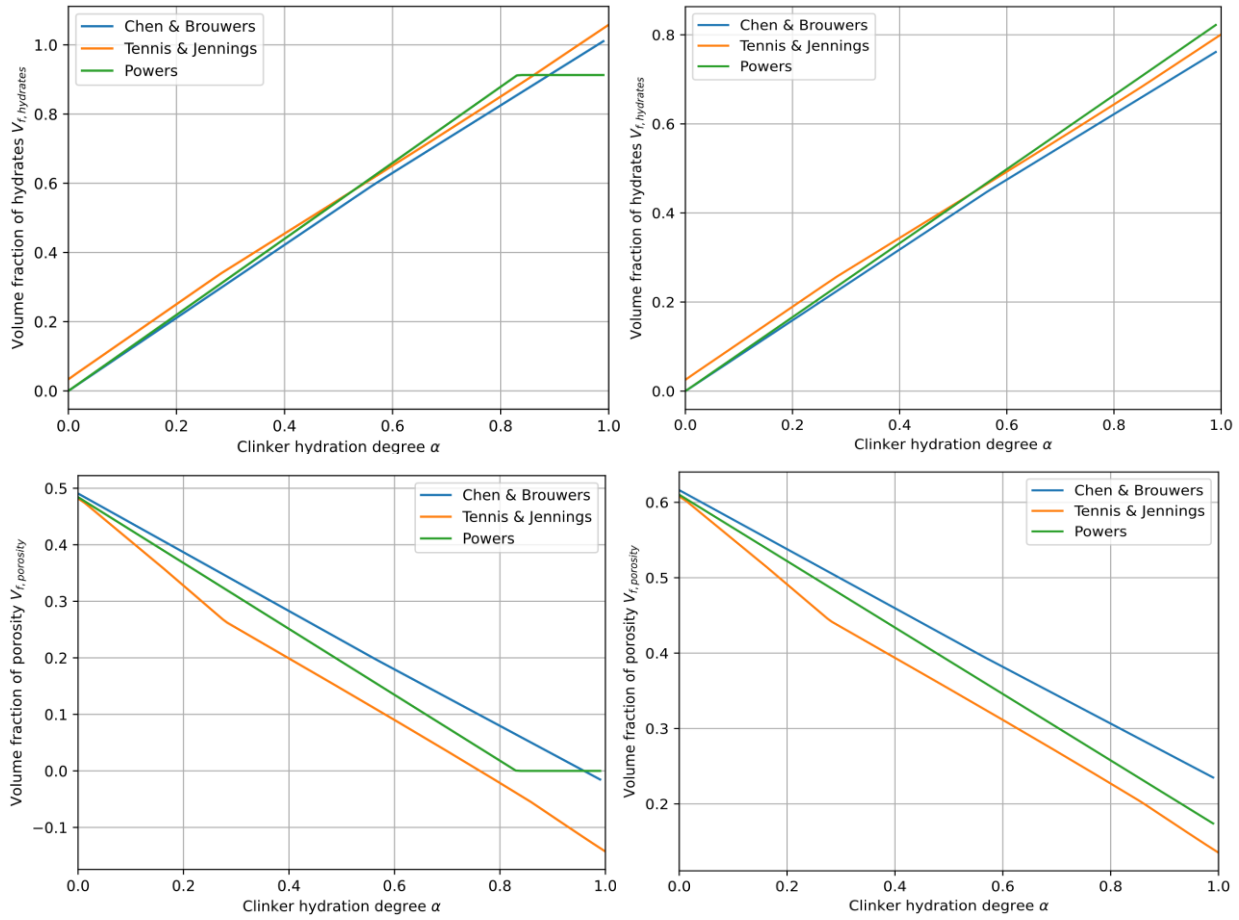


Figure 44: Comparison between the evolution of hydrates and total porosity of Chen & Brouwers' model, Tennis and Jennings' model, and Powers' model for the composition presented in Table 20, with slag substitution rate equal to 50%, a water to binder ratio equal to 0.3 (left) and 0.5 (right) and at a temperature equal to 25°C.

Figure 44 shows a good comparison between the models, for different water to binder ratio for CEM I, aimed at validating the use of the Chen & Brouwers model in place of the Powers model for future applications. The primary conclusion is that, for the same degree of hydration, both models yield comparable results, particularly in predicting hydration phases' volume fractions for CEM I. This is particularly important as many existing multi-scale models rely on the Powers model for simulating cement hydration. The results shown in the figure confirm that adopting the Chen & Brouwers model would not significantly affect the volume fraction predictions, thereby reinforcing its validity as an alternative for CEM I hydration modeling.

Validation of the developed coupled model further includes comparison with experimental data obtained by Mohamad Ali Ahmad at various hydration ages (7, 28, 56, 90, 180, 270, 360 days) for the composition outlined in Table 20. This composition features a slag substitution rate of 0, 30%, 50% and 80%. A water-

to-binder ratio of 0.5 was taken, and with a curing temperature of 25°C. The results are presented in Figure 45.

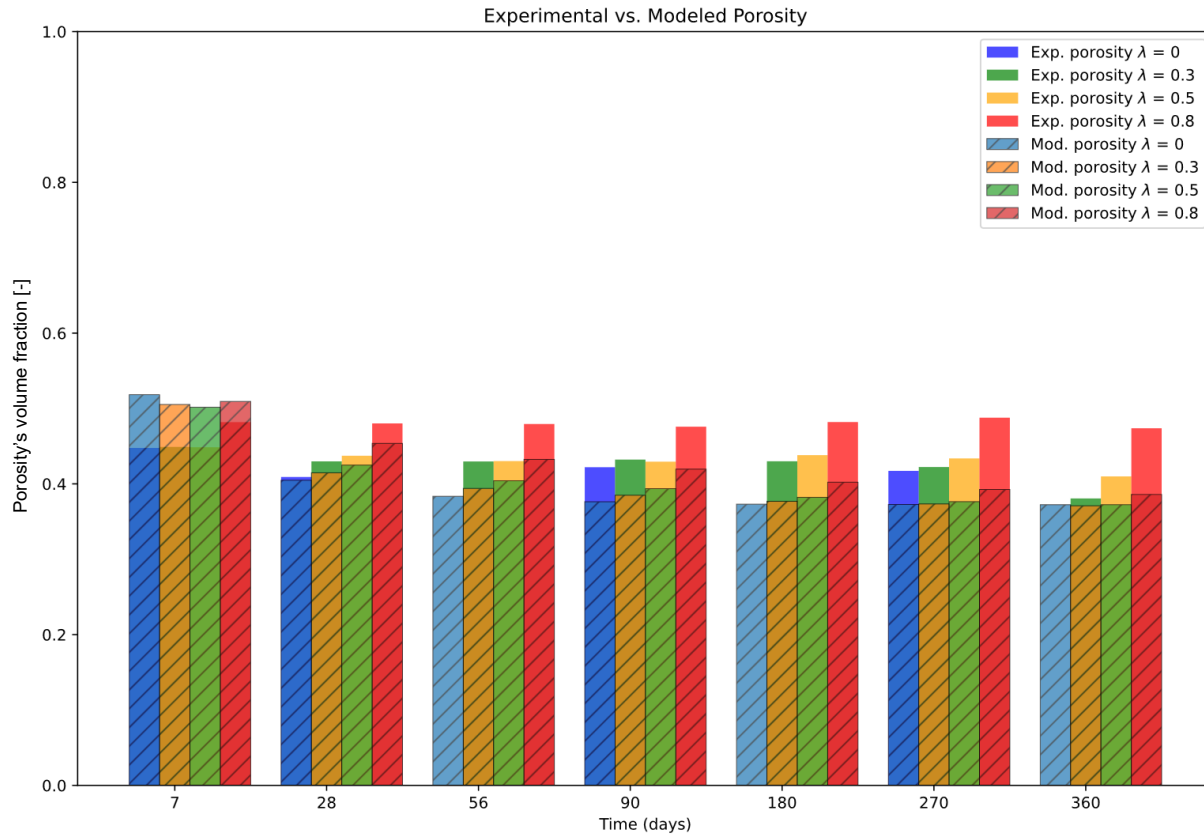


Figure 45: Comparison of the modeled total porosity with experimental data provided by Ali Ahmad [94], at different age of hydration and different slag substitution rate.

Figure 46 represents the evolution of the total hydration degree of the same slag blended cement pastes ($w/b=0.5$, $\lambda=0, 0.3, 0.5$ and 0.8 , $T=25^{\circ}\text{C}$, chemical composition from Table 20) modeled and experimentally given by Ali Ahmad [94]. The model gives reliable results upon comparison with experimental values, but overestimates the overall hydration degree for the paste with high slag substitution (equal to 0.8).

Another validation of the model involved comparing the evolution of the portlandite mass fraction with the experimental data from Ali Ahmad [94] for various slag substitution levels ($\lambda = 0, 0.3, 0.5$, and 0.8). The results (Figure 47) demonstrated a strong correlation between the model predictions and experimental findings, further reinforcing the reliability of the proposed adapted coupled model.

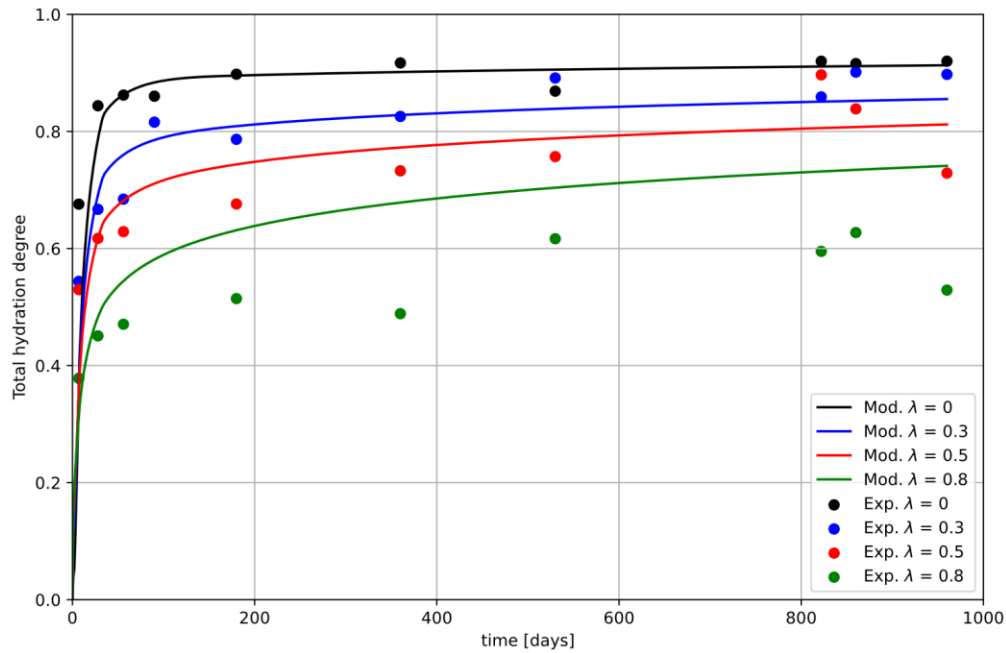


Figure 46: Comparing the evolution of the total hydration degree modeled using the developed model with experimental results obtained by Ali Ahmad [94].

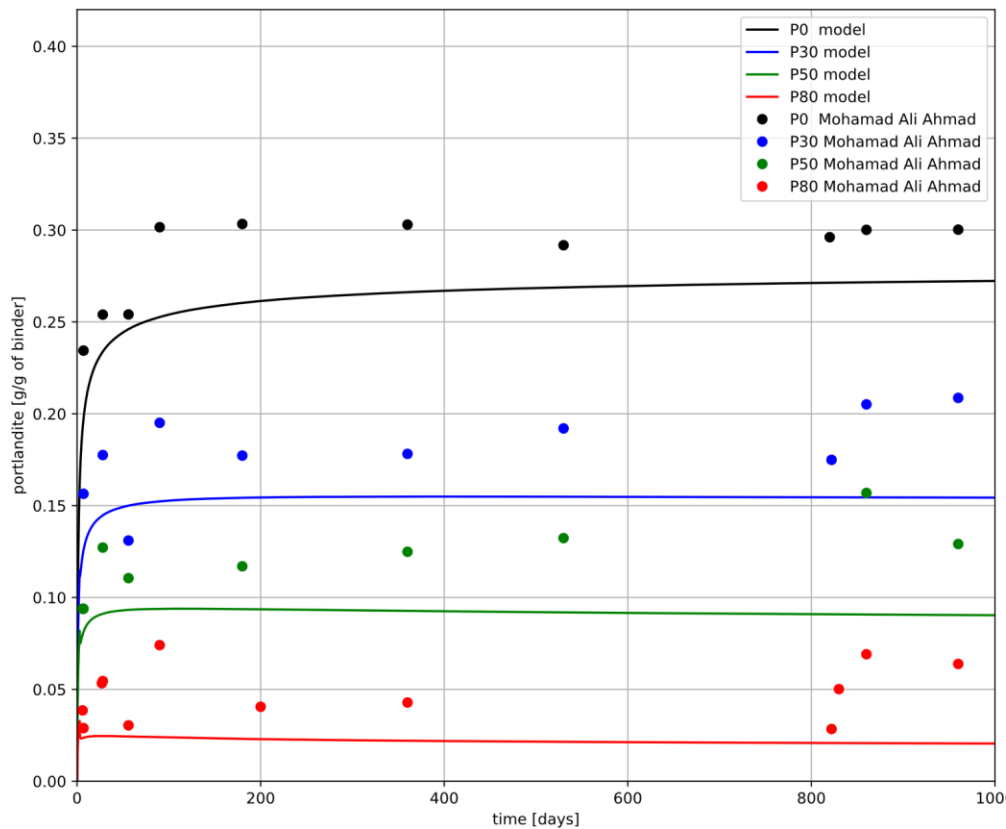


Figure 47: Comparing the evolution of the portlandite mass fraction modeled using the developed model with experimental results obtained by Ali Ahmad [94].

IV.3- Conclusion

This chapter presents the development of an analytical model designed to capture the hydration behavior of slag-blended cement over time. It combines stoichiometric relations from the Chen & Brouwers model [64] with kinetic approaches to capture the reaction rates of slag and clinker to accurately describe the time-dependent evolution of hydration phases. For clinker hydration, Bernard's model [10] is employed to simulate the hydration kinetics of individual clinker phases, ensuring accurate representation of their temporal evolution.

To address slag hydration, a newly developed model based on Knudsen's equation is proposed that takes several mixture parameters into consideration [153]. This model is calibrated using an extensive dataset and rigorously validated, demonstrating its reliability in capturing the slag hydration process. The results obtained from this analytical model serve as essential input parameters for the multi-scale diffusion model developed in Chapter VII.

Having established a clear understanding of the evolution of hydration phases, the next step is to examine the microstructural characteristics of these phases. This investigation is crucial for employing the hydration results to develop a multi-scale diffusion model that is based on experimental observations and can more accurately reflect real slag blended cementitious systems.

Chapter V

Microstructural properties of slag based cementitious materials

In the process of developing a multi-scale diffusion model that incorporates the previously established hydration model to predict the diffusion coefficient of slag-blended cement pastes, it is essential to first gain a comprehensive understanding of the microstructure of these pastes. By integrating insights from hydration reactions (specifically the types and quantities of hydrates produced) with morphological observations, this chapter establishes a solid foundation for a reliable multi-scale diffusion model. Essential input parameters for this multi-scale diffusion model include the volume fractions of hydrated phases, their shapes, and the diffusion coefficients of each phase. Additionally, the upscaling process between different levels must accurately represent the actual size scales of each hydrate phase, ensuring the model effectively predicts the diffusion properties of slag-blended cement pastes. This chapter presents morphological observations of crystalline hydrates, C-S-H phases, and the various porosity characteristics unique to slag-blended cement pastes. These observations, combined with the quantification of hydrated phases using the model developed in the previous chapter, will allow for the creation of a reliable diffusion model for slag-blended cement pastes.

In such description of microstructural properties of hydration phases, we will focus on size scales, shapes, and organizational orientation of the hydrated phases:

- (1) Regarding **Size Scale of Hydrates**, the aim is to differentiate the nanoscale features from the microscale features of different phases. This disparity in size scales affects the transfer properties of the material. Therefore, detailed information on the size scale of each hydrate type allows for more accurate representation in multi-scale models.
- (2) Regarding **Particle Shape**, the specific shapes and orientation distribution of different hydrate and pore phases influence the macroscopic transport properties. The shape of hydrate particles, whether they are plate-like, needle-like, or spherical, significantly influences their connectivity and the resulting microstructure of the cementitious matrix. This in turn affects the transport and mechanical properties of the material. Thus, incorporating the specific shapes of hydrates into the multiscale models (see Chapter VII) helps in predicting the material properties.
- (3) Regarding **Phase Organization**, the aim is to understand the spatial arrangement of hydrate and pore phases to model their impact on transport properties and behavior. At different scales, the spatial arrangement and orientation of hydrate phases plays a crucial role in defining the material's properties. The organization of hydrates can influence the development of the pore structure and the connectivity of pores which affect transport properties. At larger scales, the alignment and orientation of hydrate crystals can affect the overall mechanical integrity and durability of the material.

Figure 48 illustrates the evolution of cement hydration at the micrometric scale. At the initial state, unhydrated cement grains are surrounded by water. As hydration progresses, hydration products, primarily calcium silicate hydrate (C-S-H), form around the cement grains, depicted by yellow layers surrounding

the gray circles. This intermediate stage shows the growth of these hydration products, while crystalline hydrates, represented by green hexagons, appear within the cement paste. At the final state, the cement paste becomes predominantly composed of hydration products and pores, since unhydrated grains are almost fully reacted. This transformation to a hydrated cement paste highlights the microstructural development that significantly influences the material's mechanical properties and durability.

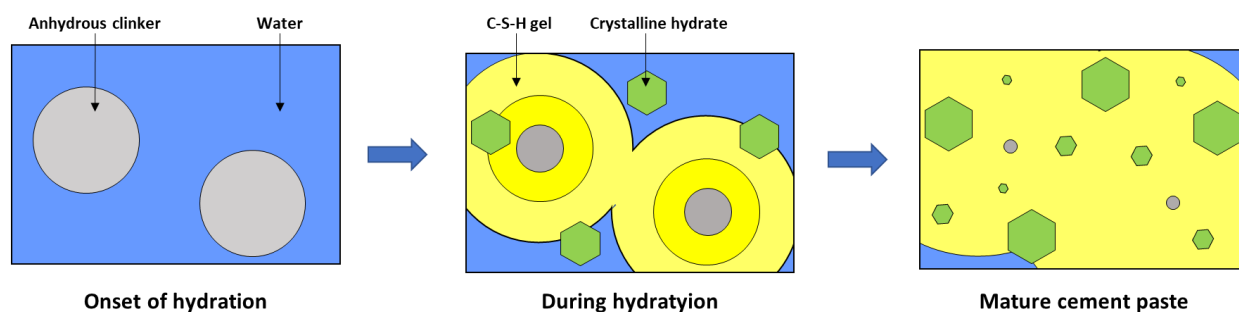


Figure 48: Schematic representation of cement paste microstructure evolution during hydration.

V.1- Solid phases microstructure

V.1.1- Morphological observations of anhydrous particles and crystalline hydrates

The microstructure of hydrated cement is a complex combination of various phases, each contributing to the overall properties of the cementitious matrix. Experimental techniques such as Nuclear Magnetic Resonance (NMR), Rietveld analysis, X Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) have been employed to investigate each specific phase in detail (see Chapter IV for the different hydrated phases). The nature of the hydrates formed is conditioned by that of the dissolved reactants, which depend on the hydration reactions of the anhydrous phases [149]. For example, Figure 49 shows the microstructural evolution of slag-blended cement pastes with varying substitution rates (30%, 50%, 70%) over hydration times ranging from 24 hours to 90 days. The darker regions represent hydrated phases, while lighter areas indicate unreacted clinker and slag particles. Early hydration (24-48h) reveals significant porosity and unreacted clinker. As hydration progresses (7-28 days), the microstructure densifies due to the formation of C-S-A-H and crystalline hydrates. By 90 days, higher slag content leads to a denser matrix with reduced porosity, illustrating the slow reactivity of slag and its influence on the cement matrix.

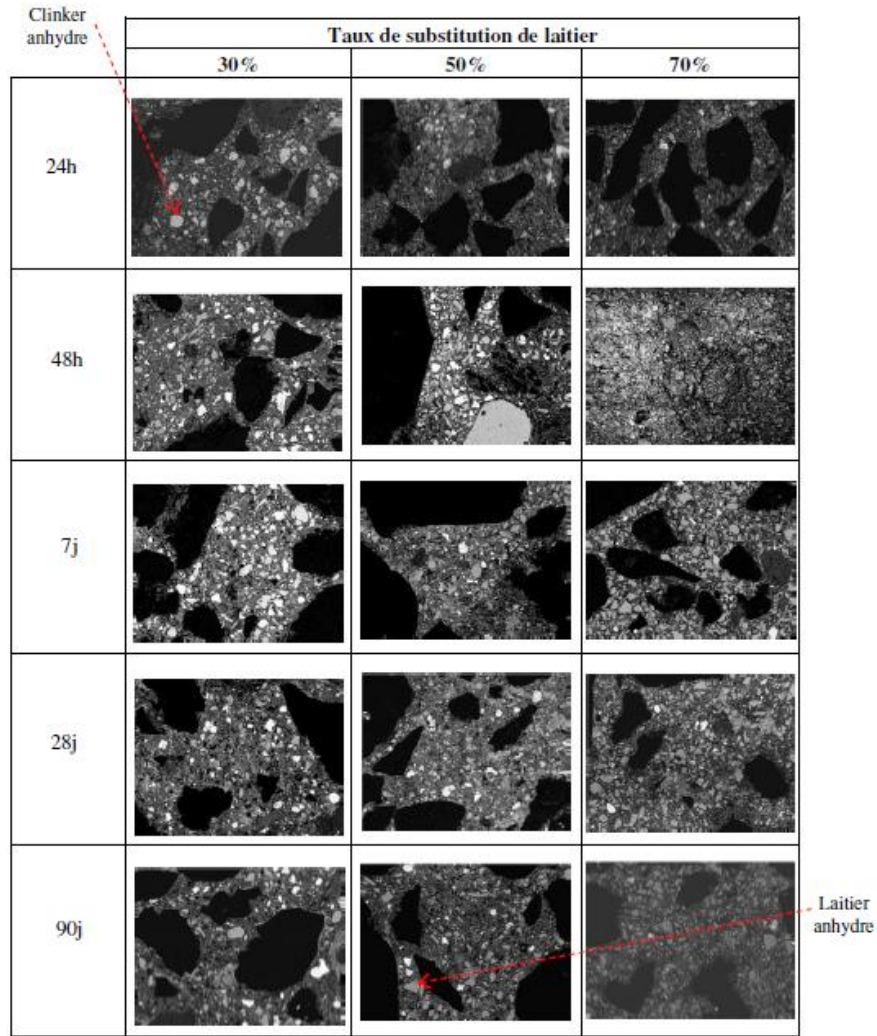


Figure 49: SEM observations to monitor the microstructure evolution of hydrating cement pastes through time [54].

Based on Scanning Electron Microscope (SEM) observations as shown in Figure 50 and Figure 51, slag and cement particles exhibit irregular shapes. To reduce computational complexity, their shapes are often modeled as spherical [8, 64, 190] to simplify computational simulations, particularly for multi-scale homogenization while providing a reasonable approximation of behavior at larger scales. To note that in modeling the unhydrated cores of cement particles, these particles are considered impenetrable, meaning that diffusion is effectively zero [190], thus chloride ions could not infiltrate these dense cores.

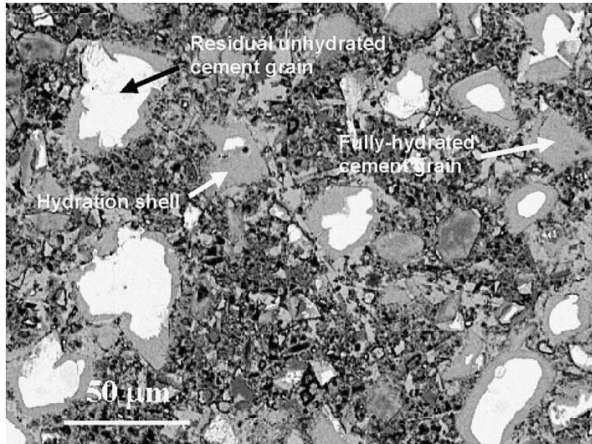


Figure 50: SEM image of OPC cement paste [191].

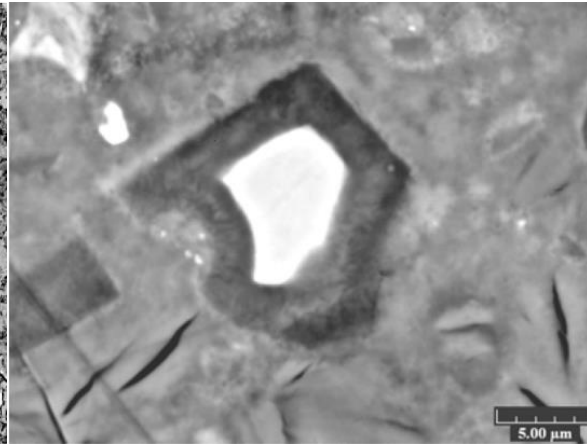


Figure 51: SEM image of partially hydrated slag grain [135].

Distinct morphological characteristics are observed in the various crystalline hydrated phases. Portlandite, a primary hydration product, transforms from its initial hexagonal plate morphology on the micrometric scale into well-oriented, more compact aggregates with reduced pore space, resulting from the growth of crystals [192–194] during hydration. This densification process is observed in both ordinary and blended cements, see Figure 52.

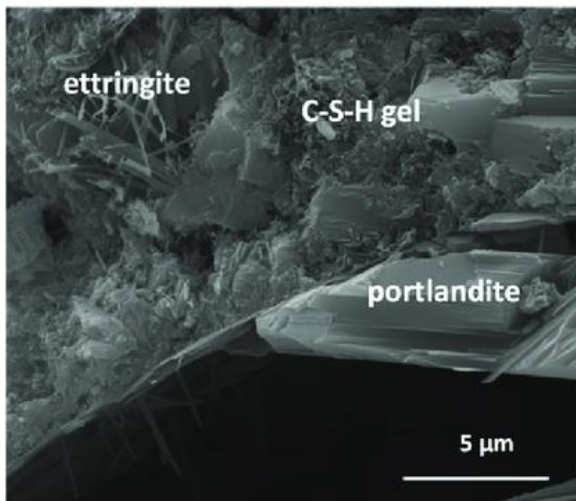


Figure 52: SEM observations of portlandite crystals in Portland and blended cement [195].

Based on experimental microscopic imaging, the tetracalcium aluminate hydrate (C_4AH_{13}) and hydrotalcite phases show a distinct hexagonal plate morphologies on the micrometric scale [196, 197] as seen in Figure 53.

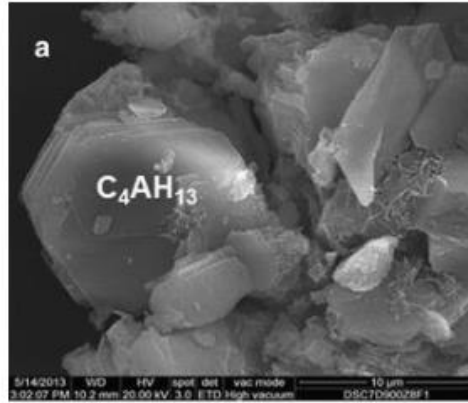


Figure 53: Microscopic observations of C_4AH_{13} crystals [196].

The AFt (ettringite) phase typically manifests as needle-like structures (Figure 54), while the AFm (monosulfate) phase exhibits flake-like or strip-like morphologies on the micrometric scale [192, 193] (Figure 55). Interestingly, AFm-like species do not intercalate within the interlayer structure of C-S-H/C-S-A-H hydrates [198].

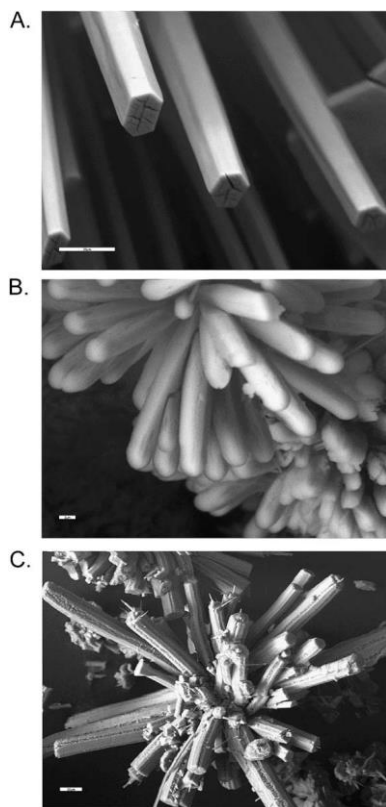


Figure 54: SEM observations of needle-like ettringite structures [199].

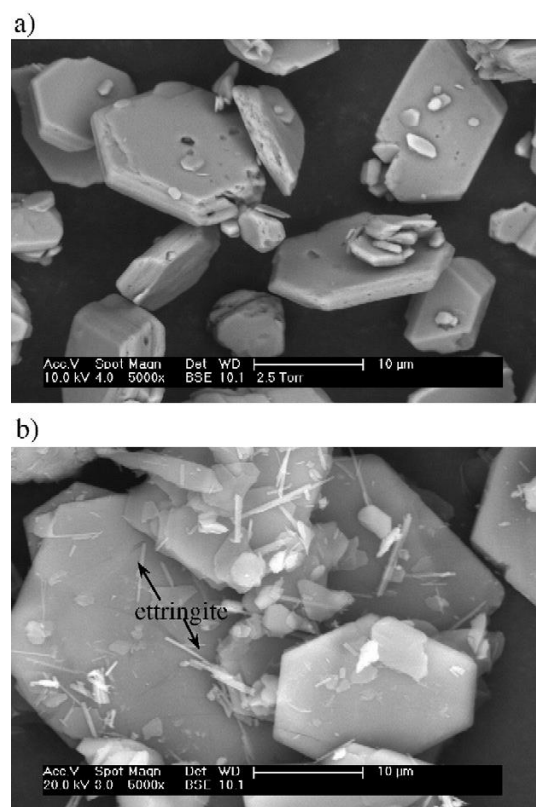


Figure 55: SEM observations of AFm crystals [200].

Monocarbonate phases are characterized by a hexagonal plate like shape [201] (Figure 56), whereas hydrogarnet phases are observed to have fibrous-like structures on the micrometric scale ranging around several tens of micrometers [202].

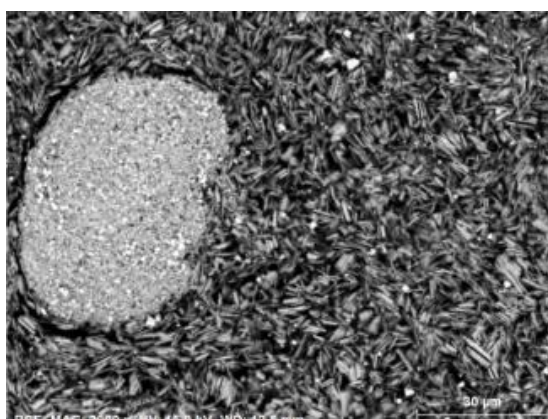


Figure 56: The morphology of the spherical monocarbonate [201].

V.1.2- Microstructural evolution of Calcium-Silicate-(Aluminum) Hydrate

With the increasing addition of slag, experimental findings [88] indicate a progressive decrease in the effective diffusion coefficient and permeability over time, which can be directly attributed to an enhancement in porosity for the same material. The reduction in these transport properties is primarily associated with a decrease in capillary porosity and a concurrent increase in nanoporosity, resulting from alterations in the microstructure of calcium silicate hydrates.

Regarding the CaO/SiO_2 and $\text{H}_2\text{O/SiO}_2$ ratios in order to calculate the molar mass or molar volume. The chemical composition of the C-S-H will be taken from the model proposed by Chen & Brouwers, as discussed in Chapter IV.

Upon hydration, cement particles undergo a dissolution due to the chemical reactions taking place, which reduces their volume. This process results in the formation of two distinct phases of C-S-H: the inner C-S-H layer and the outer C-S-H layer as seen in Figure 57.

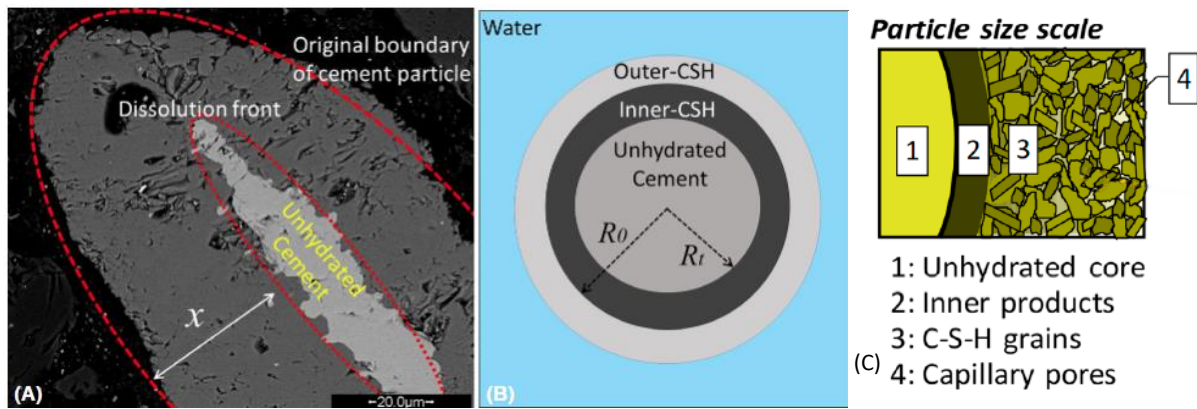


Figure 57: Experimental observation (A) [203] and schematic representation of cement grain during hydration, and the development of adjacent layers (B) [203] and (C) [204].

The inner C-S-H is a densely packed and well-organized phase that occupies the space originally held by the unhydrated cement particles.

Conversely, the outer C-S-H is less dense and more disorganized in nature. It forms in the spaces between the original cement particles and the surrounding matrix. The outer C-S-H contributes to the porosity of the hydrated cement paste, influencing the material's permeability, durability properties and mechanical properties. The outer C-S-H acts like a binding agent, holding the surrounding particles together and contributing to the overall structural integrity of the material.

Various studies [205–208] have documented that the morphology of calcium silicate hydrates is significantly influenced by the calcium-to-silicon (Ca/Si) ratio. At a high Ca/Si ratio, C-S-H typically

exhibits a fibrillar or fibrous morphology, characterized by elongated and interwoven strands as shown in Figure 58. The fibrillar-like morphology is associated with higher density and strength due to the compact and intertwined nature of the fibers, typically contributing to lower porosity of the structure. Conversely, when the Ca/Si ratio is low, the morphology of C-S-H tends to resemble crumpled foils, with thin, wrinkled layers forming a more disordered, porous and less compact structure. Further investigations [198] have revealed that the crumpled foil morphology of C-S-A-H becomes more pronounced and structurally complex with the inclusion of aluminum. The foils are observed to be thicker and longer, suggesting that aluminum incorporation plays a crucial role in altering the microstructure.

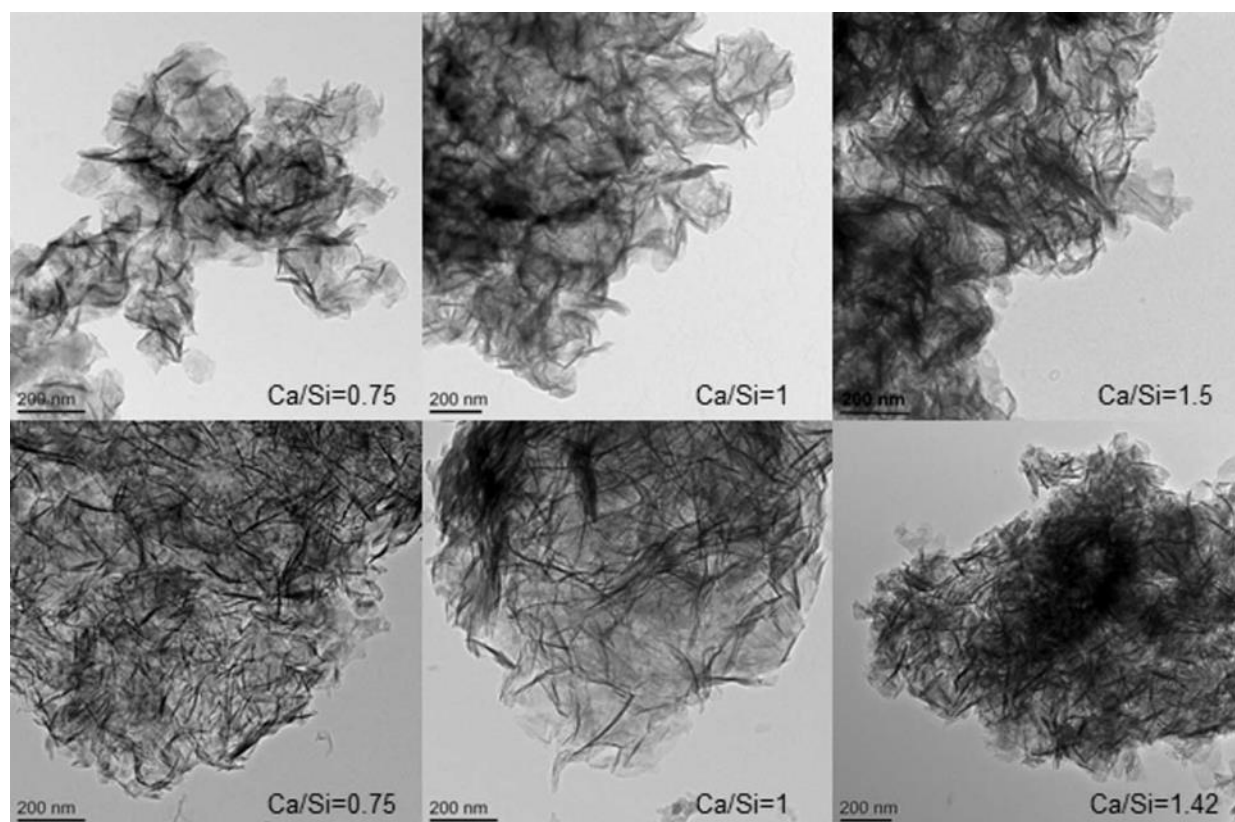


Figure 58: TEM micrographs show C-S-H samples with indicated bulk Ca/Si ratios [209].

Additionally, the mean chain length (MCL) of the calcium silicate hydrate (C-S-H) phases is observed to increase with the inclusion of slag [207, 210]. This increase in MCL due to the lowering of the Ca/Si ratio, indicates a more crystallized and robust C-S-H structure, contributing to the overall change in the cementitious material. These microstructural enhancements contribute to an improvement of durability properties of the cementitious matrix.

At a lower scale, the microstructure of Calcium Silicate Hydrate gel, is often represented as detailed by Feldman and Sereda [211] in Figure 59. It reveals a complex, layered arrangement characterized by diverse pore types and water distribution. The structure of the gel consists of C-S-H sheets interspersed with

interlayer and interstitial pores, which contribute to its overall porosity. Interlayer pores, located between the C-S-H sheets, contain interlayer water. Additionally, water molecules adsorb onto the surfaces of the C-S-H layers, enhancing the interaction between the sheets [70, 212–214].

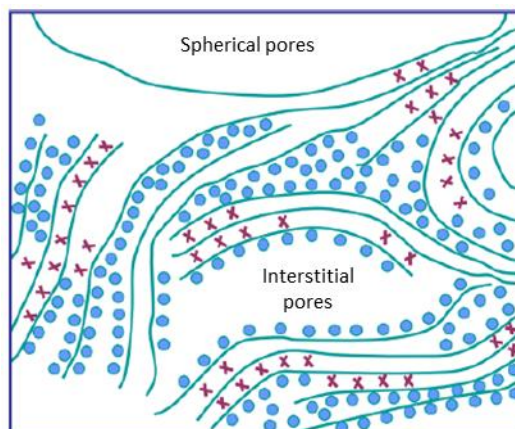


Figure 59: Schematic representation of C-S-H and intersheet and interstitial porosity by [211, 214].

The incorporation of slag into cementitious materials has been shown to significantly enhance the confinement of the cementitious matrix [204]. This densification is attributed to several key microstructural changes. Firstly, the presence of slag increases the tortuosity of the pore network, making it more difficult for aggressive agents such as chloride ions to penetrate the concrete. Secondly, the specific surface area within the micro-pores is substantially higher [205, 206], which enhances the capacity for physical and chemical interactions within the cement matrix.

V.2- Porosity

V.2.1- Experimental procedures for measuring porosity in cementitious materials

During hydration, water integrates in the cement matrix, at different scales, whether physically or chemically bound. Using different experimental techniques, different porosities indicators can be found. The total porosity can be determined experimentally according to the procedure described in AFREM AFPC [215] by hydrostatic weighing. The capillary water absorption test allows us to measure water absorbed in the pores of the samples according to NF P18-459, 2010 [216]. Mercury intrusion porosimetry is used for determining the pore size distribution and pore volume as a function of pore access thresholds. It consists of penetrating a non-wetting liquid (mercury) into the open pores of a dried sample, under applied pressure [217].

V.2.2- Porosity Classification and Modeling in Cementitious Materials

Different researchers have categorized porosity based on pore size, through various nomenclatures and classification systems. This section reviews the definitions and classifications of porosities according to

different authors, namely Mindess et al. (2002) [218], Mehta (1986) [219], and the IUPAC [219–223] as depicted in Figure 60. Additionally, we discuss the subdivision of pores based on mercury intrusion porosimetry, according to Wang [49].

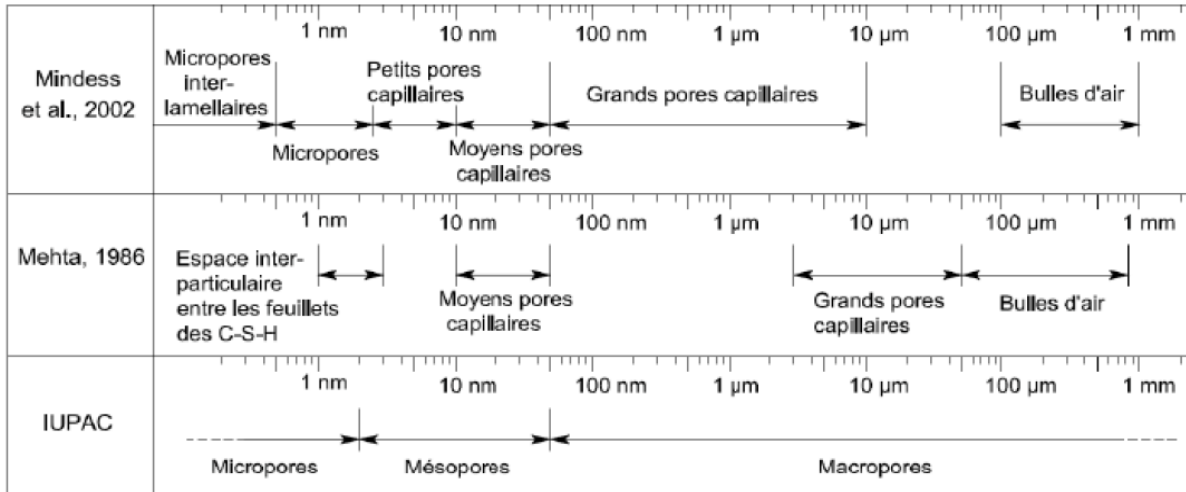


Figure 60: Different porosities classification and nomenclature [224].

Mindess et al. [218] provided a detailed classification of pores based on size ranges. They identified large capillary pores as those ranging from 50 nm to 10 µm. Pores smaller than this were further categorized into medium capillary pores (10 nm to 50 nm), small capillary pores (2.5 nm to 10 nm), micropores (0.5 nm to 2.5 nm), and interlamellar micropores, which are even smaller [225]. Mehta's classification focuses on the interparticle space within the C-S-H structure. The author identified inter-particle pores in C-S-H as those ranging from 1 nm to 3 nm. Medium capillary pores were defined as those between 10 nm and 50 nm, while large capillary pores were classified as ranging from 3 µm to 50 µm. The IUPAC provides a standardized classification of pores into three categories: micropores, mesopores, and macropores. Micropores are those smaller than 2 nm, mesopores range from 2 nm to 50 nm, and macropores are those larger than 50 nm. This classification is widely used due to its simplicity. Other researchers [226–228] have also adopted alternative classifications of porosity in cementitious materials. For instance, these studies have subdivided pores into gel pores (0–10 nm), fine capillary pores (10–50 nm), medium capillary pores (50–100 nm), large capillary pores (100 nm–10 µm), and macro pores (>10 µm). These classifications are different interpretations of the complex porosity characteristics in cement-based materials.

Stephant's analysis [88], as presented in Figure 61, (as well as others [49, 229, 230]) identified three distinct porosity modes based on peaks observed in mercury intrusion porosimetry graphs:

1. First Mode (100–1000 nm): This mode is characterized by pores initially present between anhydrous cement grains, partially filled by hydrates. These pores are associated with the water

initially occupying the space between cement grains. The volume and size of these pores decrease during hydration as hydrates develop and fill the space.

2. Second Mode (10–100 nm): Known as the inter-hydrate mode, these pores are attributed to spaces between hydrates. This porosity mode corresponds to the residual porous network after the formation of external hydrates, indicating voids between hydrates.
3. Third Mode (<10 nm): The intra-hydrate mode represents the smallest pores, located within the crystallites of C-S-H gel. This porosity mode is not detectable by mercury intrusion due to its small size [193].

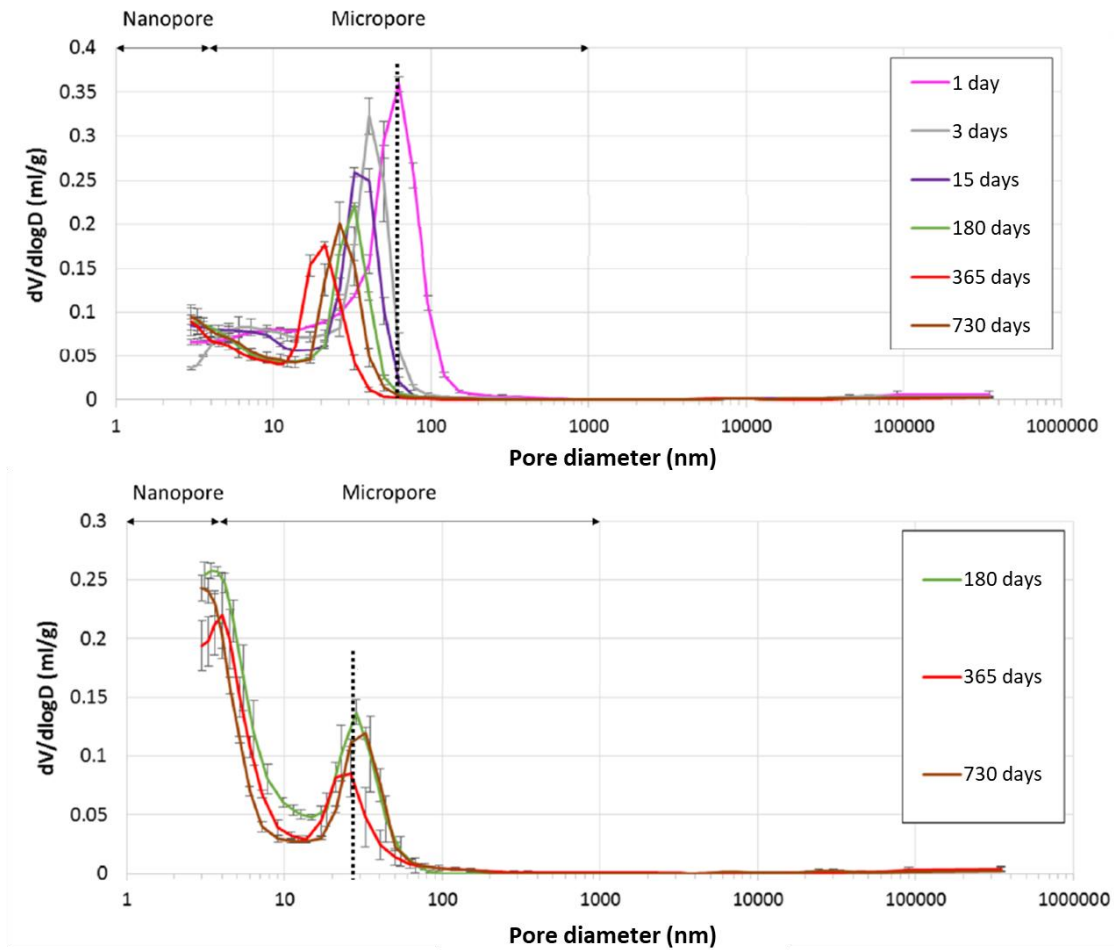


Figure 61: Porosity repartition of cement pastes for OPC (top) and slag substitute cement (bottom) [88].

The classification of porosity in cementitious materials varies among different researchers, with distinctions made based on pore size and their spatial distribution. The comprehensive understanding of porosity types, from large capillary pores to intra-crystallite pores, is essential for predicting the mechanical performance and durability of cement-based materials.

Several empirical models have been developed over the years to describe the evolution of porosity in OPC cement materials. Notable contributions in this area include works by Hansen (1966), Balshin (1949), Ryshkewitch (1953), Powers (1960), and Kadlecěk (1973) [231–235].

Empirical models provide a foundation for understanding how porosity evolves during the hydration process and how it affects the overall properties of cementitious materials. These models, developed through extensive experimental research, offer valuable insights into the relationship between porosity and material performance [231, 234, 235]. Ranaivomanana et al. [225] (inspired by Maekawa et al. [236]) proposed a model to predict the evolution of the porosity network and pore sizes distribution for OPC cements. This model is based on the pore size classification, established in literature as seen in section V.2.2-.

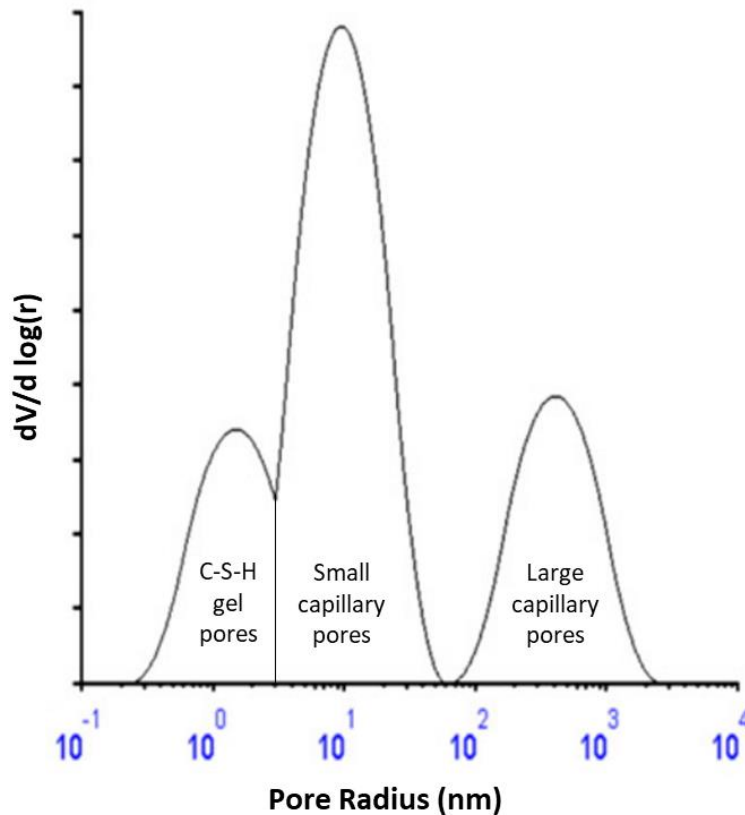


Figure 62: Classification of Porosity Types and Size Ranges According to Ma et al.(2014) [190] and Ranaivomanana et al.(2011) [225].

Ma et al. [190] developed a numerical model to calculate the evolution of the porosity network (the volume fraction of gel pores, small capillary pores and large capillary pores) in function of the cement hydration degree (Figure 63). It is assumed that capillary pores do not exist within the inner hydration product layer inside the initial boundary of the cement grains. The outer C-S-H layer is characterized by multiple porosity types (small capillary pores and gel pores) [190, 205]. For the purposes of water transfer

modeling, air bubbles are ignored as they are considered to reside at another scale [229, 237] without substantially affecting the accuracy of the predictions [190, 204].

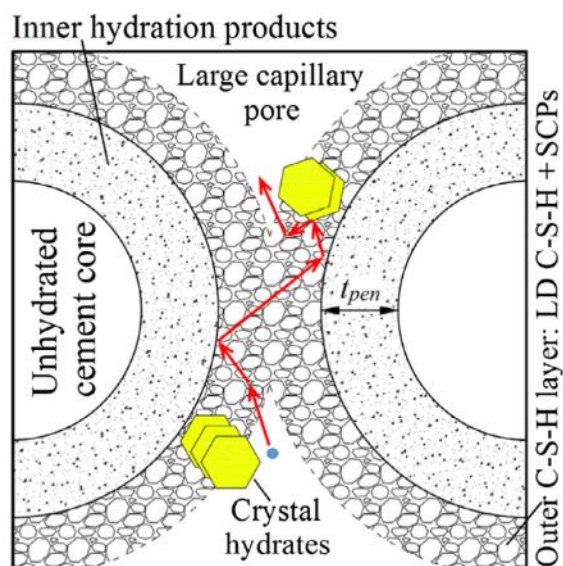


Figure 63: Ma et al. [190] representation of hydration products and porosities.

The analytical equations utilized to quantify the proportion of small and large capillary pores through hydration, initially formulated by Ma et al. [190] and subsequently expanded upon by Achour [8], have been further modified to accommodate slag-blended cements and are provided in Appendix B. This distinction between small and large capillary pores is further used in the developing of a variant of the multi-scale diffusion model presented in Chapter VII. Further conclusions and insights drawn from applying this improved capillary pore distinction will be elaborated in Chapter VII, where the outcomes of the multi-scale diffusion model are presented.

V.2.3- Effect of slag addition on porosity

The inclusion of ground granulated blast furnace slag (GGBFS) in cement mixtures results in a notable decrease in the effective diffusion coefficient. The densification of the cement mix microstructure due to slag addition results in higher tortuosity and an increased specific surface area within the micro-pores, significantly impeding the ingress of harmful agents like chloride ions [90, 205, 206]. The variations in the effective diffusion coefficient with slag content are linked to the decreased capillary porosity and increased volume of nanopores [88]. It is important to note that regardless of the presence of slag in the mixture, the effective diffusion coefficient decreases over time due to the gradual filling of capillary porosity [208, 238].

As the slag content in the cementitious mix increases, the hydration reactions produce a denser and more refined microstructure. This is due to the pozzolanic reactions between the slag and the calcium hydroxide

generated during cement hydration, which result in the formation of additional C-S-A-H phase. While the total porosity remains the same or sometimes increases, these newly formed C-S-A-H fill the capillary pores, thus reducing the overall capillary porosity [88, 206]. At the same time, the microstructure becomes more compact with a higher volume of nanoporosity, contributing to the densification of the cement paste. The densified matrix with reduced capillary porosity limits the ingress of aggressive agents such as chloride ions, thereby enhancing the material's diffusion coefficient.

The refinement in porosity (see Figure 61), rather than total porosity, is assumed responsible for the observed reduction in the diffusion coefficient [88]. Specifically, a variation in the pores smaller than 50 nm is noticed and is primarily responsible for the reduction of the diffusion coefficient in slag-blended cement paste [192]. The same result was observed by El Achrafi [206] see Figure 64. The figure illustrates that after six years, the incorporation of slag in cement results in a shift of the porosity peak towards smaller pore diameters (<10 nm).

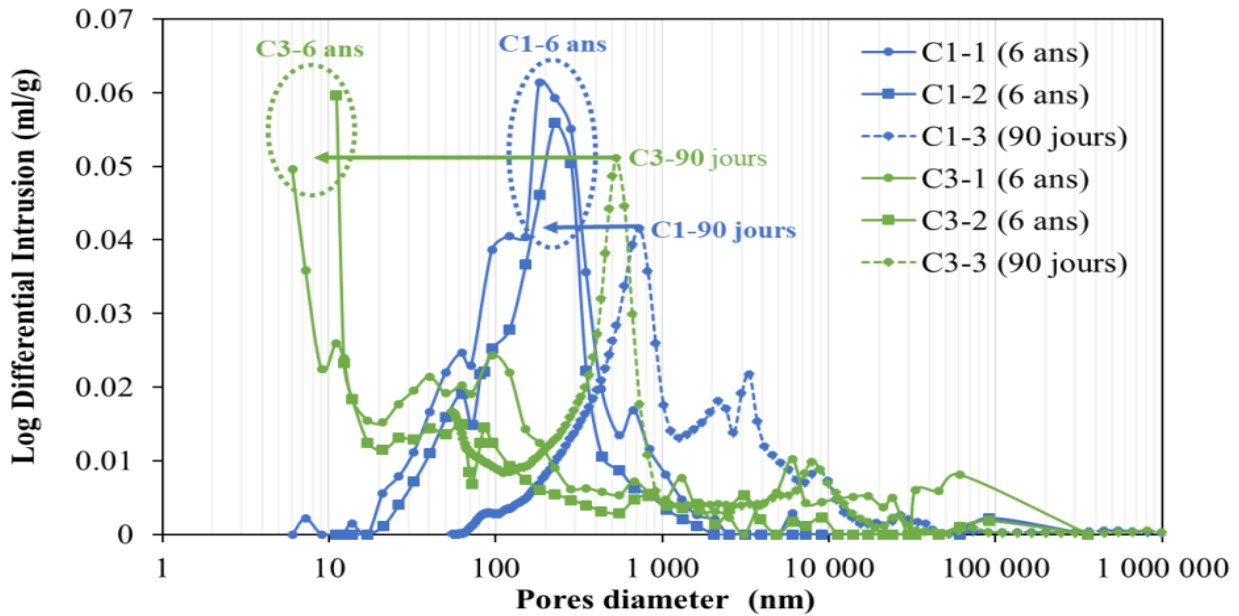


Figure 64: Mercury intrusion porosimetry results by Al Achrafi [206] showing the effect of slag on porosity distribution. (C1: OPC concrete, C3: slag blended concrete, slag substitution rate =62%).

This highlights the relevance of the work of Ma et al. [190] presented in section V.2.2- and its extension to slag-blended cement presented in Appendix B, as it provides a useful quantification of the porosity fraction below 100 nm.

V.2.4- Evolution of porosities through time

As hydration progresses, the total porosity of cement diminishes due to the hydration reactions. This process results in a reduction in the volume of large pores, while the volume of smaller pores remains

relatively constant [239]. In general, for a cement with no slag substitution, a 5% reduction in water-accessible porosity (measured by drying at 105°C) was observed [26] between seven days and three months of hydration. Kocaba (2009) [27] reported a decrease in porosity from 56% to 43% for CEM I cement paste, indicating a reduction in pore volume and refinement of mercury-accessible pores during hydration [206].

However, at 28 and 90 days, the pore sizes in slag cement paste are finer, and the microstructure is refined due to slag hydration reactions [240].

For CEM I cement, water desorption test shows that after six months and two years of hydration, the pore size distribution remains similar, indicating near-complete hydration by six months [88] as shown in Figure 65. When comparing with CEM III/C curves at extended hydration periods, it becomes evident that the addition of slag results in a noticeable reduction in pore diameters, enhancing the densification of the microstructure.

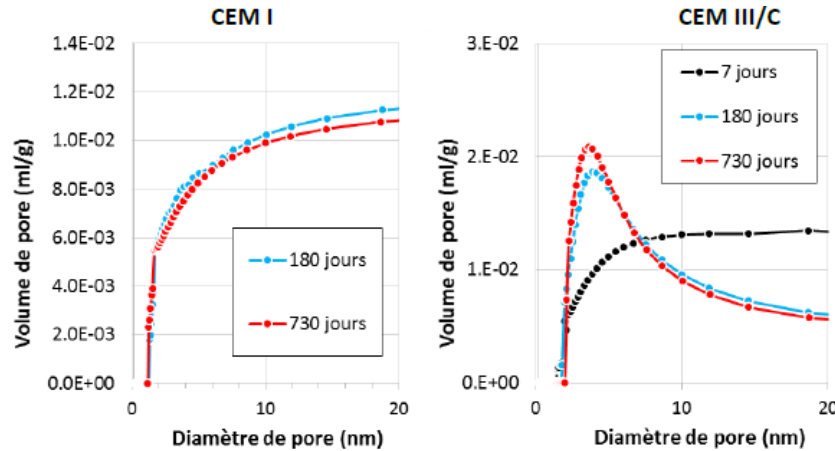


Figure 65: Pore size distribution for cement with and without slag at different hydration time by Stephant [88].

Studies have shown that substituting cement with slag slightly shifts at an early age (28 days) the main pore mode to a larger diameter while reducing the size of pores as slag content increases [217, 239, 241] see Figure 66.

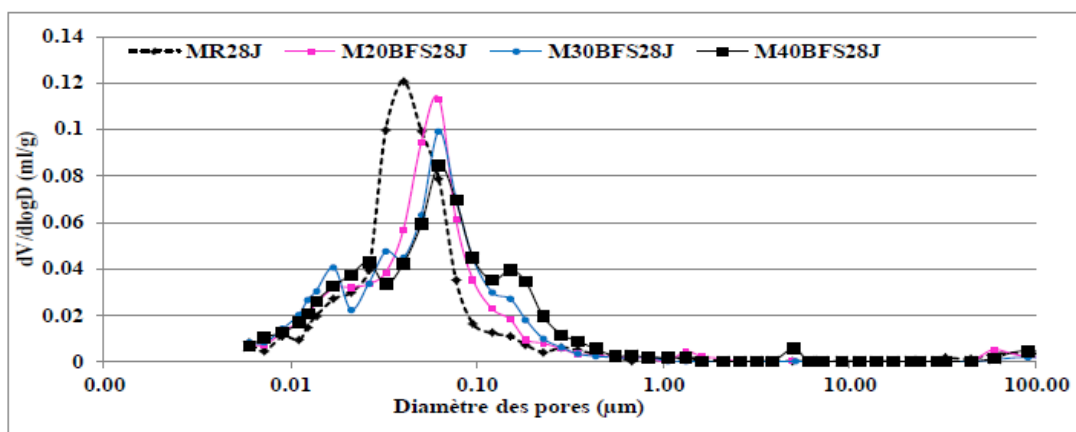


Figure 66: Porosity distribution when substituting clinker with 20, 30 and 40% of slag at 28 days [217].

The incorporation of ground granulated blast furnace slag (GGBFS) into Portland cement generally results in an overall increase in porosity [27, 54, 56] for non-mature pastes. For a given degree of hydration, the porosity in slag-blended cements can be comparable to or even higher than that in CEM I cement [88]. The increased early-age porosity in blended systems is attributed to their lower clinker content and the slower reaction kinetics of slag [242, 243].

To conclude, at later ages, studies report smaller pore entry sizes for blended cements [88, 242–245]. The volume of large pores decreases more significantly over time for slag blended cement than for ordinary cements, resulting in comparable total porosity at long term hydration [239]. When comparing slag-blended and Portland cements, total porosity decreases with hydration progression in both cases, but pore size distribution shifts to smaller sizes in slag cements [239].

V.2.5- Specific Surface Area

The reduction in pore size leads to an increase in specific surface area and a decrease in pore connectivity [59, 88, 238, 246]. This variation is directly related to the content and microstructure of the C-S-A-H phase [88]. As hydration progresses, the volume of capillary pores continues to decrease, and their size stabilizes after a few days [208]. Concurrently, the amount of gel porosity sustains, implying the formation of a more compact product with an increased bulk density of the C-S-A-H gel.

The accessible capillary porosity decreases with the addition of slag. It has also been shown that slag addition increases the critical entry diameter of nanopores and the volume of nanopores, likely due to a higher quantity of C-S-A-H and lower density of these phases [88]. During hydration, the coefficient should decrease as the material's porosity decreases and refines [247, 248].

Finally, Slag addition does not significantly affect bound water content or chemical shrinkage [88]. Various configurations tested by Wong et al. demonstrated a reduction in permeability with slag addition, attributed to pore structure refinement as with diffusion [249].

V.2.6- Ionic Composition and Diffusion

Ionic diffusion primarily occurs in the liquid phase within the material. The composition of the pore solution is a factor influencing the diffusivity of porous cementitious materials that significantly affects how ions move through the material [250, 251].

Ionic movements are driven by concentration gradients and electrical potential differences, forming the basis of the Nernst–Einstein equation used to evaluate diffusion transport properties in cementitious materials [252]. It is notable that the pH in Portland cement ranges from 13 to 13.5, whereas it is lower in slag cements [27]. This may be due to the C-S-A-H gel in hydrated slag cement that has lower calcium-to-silicate ratios and higher aluminum content, potentially enhancing alkali-binding capacities [253, 254].

There are several established models for calculating ionic composition and quantifying alkali concentrations in cement binders. These models can be categorized into empirical models, such as those developed by Popovics (1998) [255], and analytical models, including those proposed by Taylor (1990) [256], Kim and Hong (2001) [257], Rivard et al. (2003) [258], Brouwers and Eijk (2003) [259], and Chen (2007) [51]. These models could potentially be used to calculate the ionic composition, which may be a factor influencing the diffusion coefficient in slag-blended cement. However, this aspect will not be addressed in this work.

V.3- Conclusion

To summarize the microstructural representation of the hydrated solid phases, Table 21 synthesizes the experimental observations regarding their morphology. The geometrical aspect ratio ω representing the geometrical shape of the inclusion are also indicated (more information about the aspect ratio is provided in Appendix C).

Hydrate	Morphology	aspect ratio ω
Anhydrous cement particles	spheres	1
Anhydrous slag particles	spheres	1
Portlandite	hexagonal plate /well-oriented compact aggregates	<1
Tetracalcium aluminate hydrate	hexagonal plate	<1
hydrotalcite	hexagonal plate	<1
AFt (ettringite)	needle-like structure	>1
AFm	flake-like or strip-like structure	<1
Monocarbonate	spheres	1
hydrogarnet	fibrous-like structures	>1
C-S-A-H	At high Ca/Si ratio, fibrous morphology (elongated)	Variable depending on the scale
	At low Ca/Si ratio, crumpled foils, with thin, wrinkled layers forming a more disordered, porous and less compact structure	

Table 21: Summary of the solid phases microstructure as observed experimentally.

The incorporation of slag as a substitution in cementitious materials influences the quantity and formation kinetics of hydration phases, resulting in variations in porosity. This differentiation in porosity arises from the distinct morphologies of the hydrated phases formed during the hydration process, leading to altered microstructural characteristics in slag-blended cement.

The examination of porosity in slag blended cementitious materials reveals significant impacts on the material's microstructure and transport properties. The inclusion of slag notably reduces the effective diffusion coefficient, primarily due to the refinement of the pore structure and the densification of the material over time. This reduction is primarily observed in the capillary pores, which progressively decrease in size as hydration progresses. Empirical and numerical models, such as those proposed by Ma et al. [190] provide useful tools for predicting the evolution of porosity based on cement hydration.

The classifications of porosity vary among different researchers but generally converge on the division between gel pores, capillary pores, and macropores, with slag cements showing a particular tendency for shifting the pore distribution towards smaller diameters over time. This microstructural refinement, particularly within nanopores, contributes to the reduction in diffusion, improving the material's long-term durability. The hydration kinetics of slag cement is slower, leading to higher initial porosity compared to Ordinary Portland Cement (OPC), but results in a denser microstructure as hydration continues.

The influence of slag on the specific surface area, pore size distribution, and microstructure highlights the importance of understanding the nuanced changes in porosity for predicting the diffusion properties of slag blended cementitious materials. As hydration advances, the reduction in large capillary pores and the formation of fine porosity, particularly nanopores, significantly affect the diffusion characteristics,

emphasizing the need for models that account for these variations when evaluating the performance of slag-blended cements.

The primary goal of this chapter is to utilize the detailed understanding of the microstructural evolution of the slag blended cementitious materials, observed through experimental studies, to develop a multi-scale diffusion model in Chapter VII. The developed diffusion model will be based on real experimental observations of hydrates morphology and material's porosity.

Chapter VI

Diffusive Properties of Slag Blended Cementitious Materials

VI.1- Chloride diffusion in cementitious materials: State of the art

VI.1.1- Problematic of chloride diffusion

The integrity of reinforced concrete structures is significantly compromised by the corrosion of steel reinforcement, a problem primarily caused by the infiltration of aggressive agents from the external environment through the concrete's porosity and cracks [260, 261]. Chloride ions, particularly present in marine environments, are among the most detrimental agents. The mechanism of their ingress varies with the saturation state of the concrete. For concrete structures submerged in seawater, where the material remains fully saturated, diffusion is the predominant mode of chloride ion transport. This diffusion process is driven by the ionic concentration gradient between the seawater and the concrete interstitial solution [252, 262] (Figure 67).

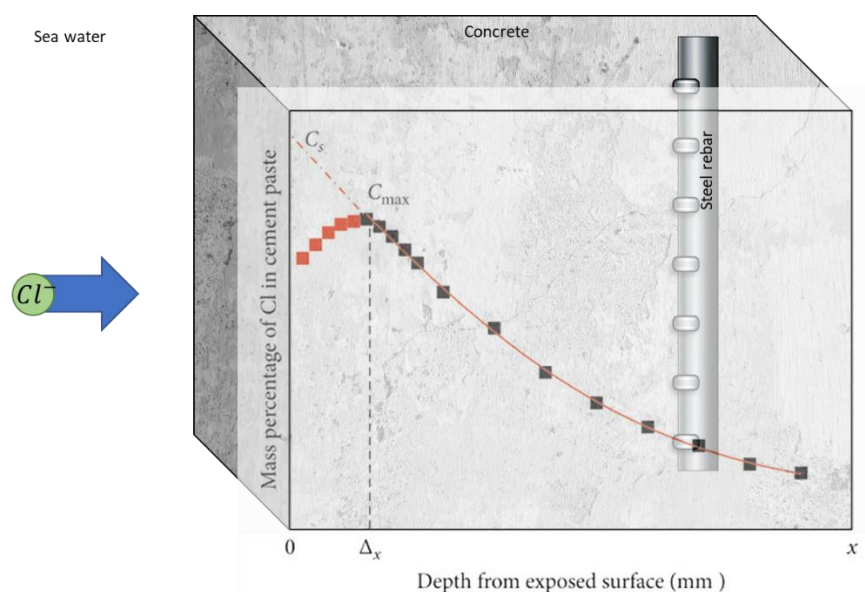


Figure 67: An example of chloride diffusion profile in the concrete cover of a steel reinforced structure.

The penetration of chlorides into concrete is influenced by material characteristics and environmental conditions, such as cyclic wetting and drying, temperature fluctuations, and exposure conditions.

All other parameters kept constant, the partial substitution of clinker by slag results in a significant decrease in the diffusion coefficient. This reduction cannot be attributed solely to the total porosity of the materials, which does not vary significantly upon substitution by slag for a given water-to-cement ratio as seen in Chapter IV.

Instead a common argument is that the refinement of porosity is primarily responsible for this decrease of the diffusion coefficient [206, 263, 264].

VI.1.2- Ion Transport Mechanisms in Saturated and Unsaturated Environments

When concrete structures are submerged in seawater, chlorides can ingress through capillary absorption and diffuse through the liquid phase within the affected zone [265]. In a saturated environment (Figure 68), chloride transport is primarily governed by diffusion, which is generally slower compared to transport mechanisms in unsaturated environments, assuming similar material properties.

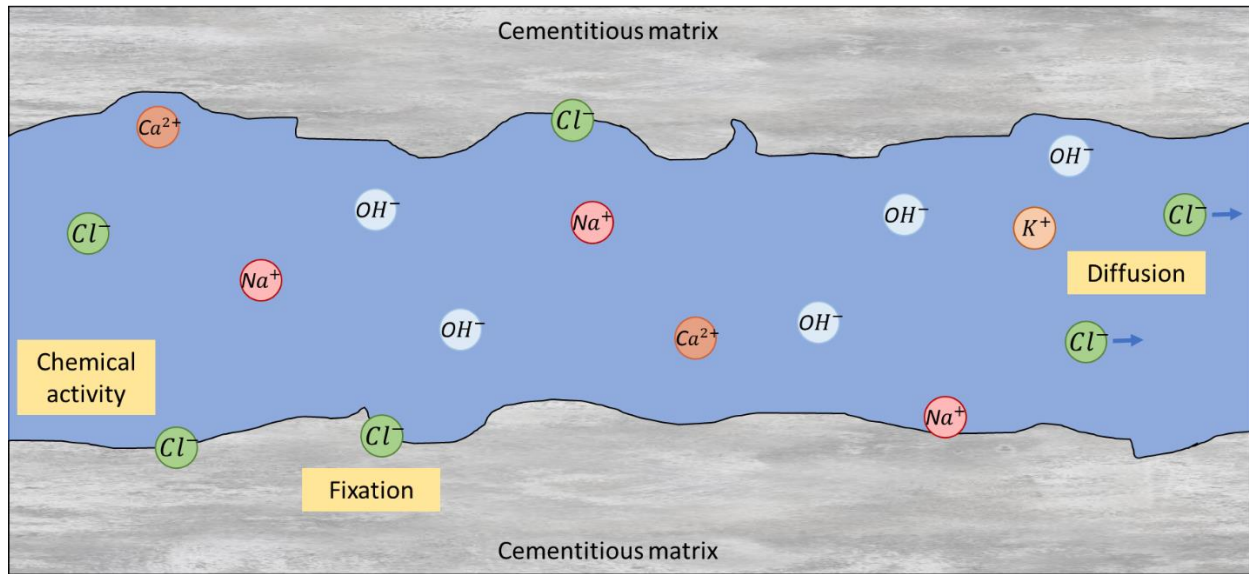


Figure 68: Ion and moisture transport in a saturated porous medium.

However, when the structure is subjected to wetting/drying cycles (e.g., tidal zones, exposure to sea spray or de-icing salts), the concrete is then considered as an unsaturated porous medium (Figure 69). In such cases, chlorides transfer through the liquid phase via advection [6] coupled with moisture transport. On one hand, when chlorides reach the concrete surface, chloride ions are advected into the concrete along with liquid water due to capillary suction forces. This convective transport is driven by the surface tension between the gas and the liquid phases in the capillary pores. The convection of liquid phases significantly accelerates chloride penetration, with a single day of saline solution wetting capable of driving chlorides deeper than several months of diffusion in a saturated environment [266].

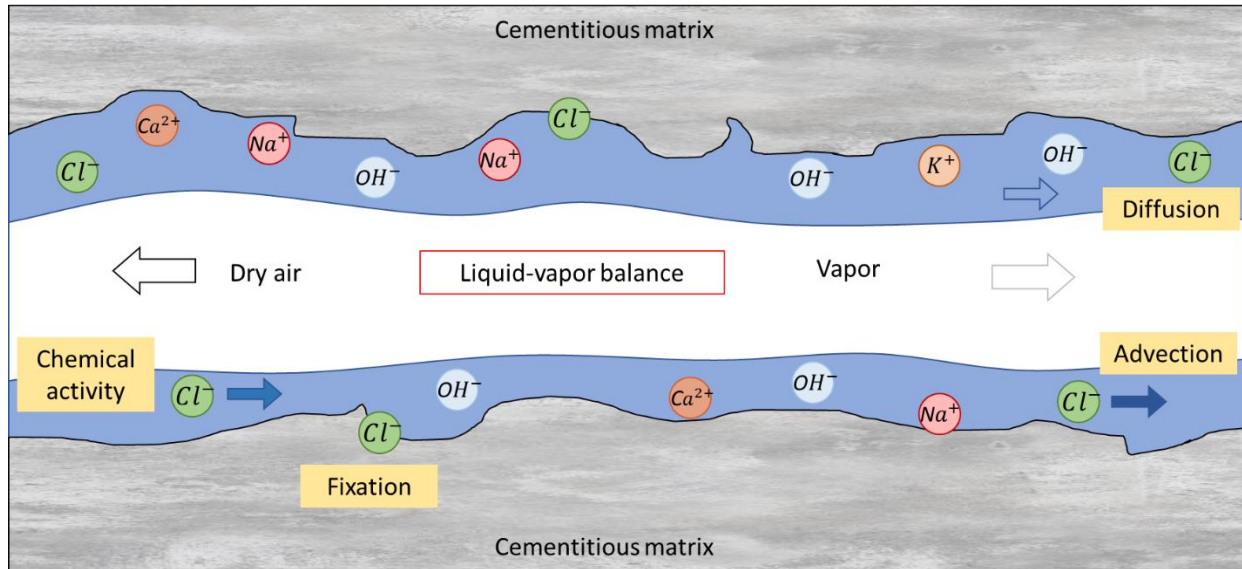


Figure 69: Ion and moisture transport in unsaturated porous media.

On the other hand, ion transport within the interstitial solution can alter water activity and modify the equilibrium between liquid water and water vapor, thereby influencing water transfer [267].

VI.1.3- Chloride Ions In Concrete

Chlorides may exist in several states within the concrete's internal structure [268]:

- Chemically bound chlorides (e.g. Friedel's salt) and physically bound through adsorption on C-S-H phases mainly and other produced hydrates (AFm, CH, ... [269]) (ionic exchange between OH⁻ and Cl⁻ ions).
- Free chlorides (in ionic form and unreacted with the cementitious matrix) in the interstitial solution of pores.

During diffusion, chlorides may chemically be bound with cementitious hydrates. These reactions are particularly notable in young concrete. Chemically bound chlorides result from reactions with cement paste, such as the formation of chloroaluminates from tricalcium aluminate C3A.

Chlorides can also be physically or chemically adsorbed onto pore surfaces within the material. Sergi, Yu, and Page (1992) [270] hypothesized that all chlorides bound in concrete result from this phenomenon and modeled chloride diffusion using the Langmuir or Freundlich adsorption isotherm. This chloride diffusion isotherm is found to be modeled differently in literature, see for example Zibara [271], Elakneswaran [272], Hirao [273], Florea [274, 275]...

In a saturated environment, the total chloride quantity ($c_{Cl,tot}$, in [mol/m³ of concrete]) is expressed as the sum of bound chloride $c_{Cl,bound}$, in [mol/m³ of concrete]) in solid phases and the quantity of free chlorides in the interstitial solution ($\phi c_{cl,free}$, with ϕ being the material porosity, and $c_{cl,free}$ in [mol/m³ of solution]):

$$c_{Cl,tot} = c_{Cl,bound} + \phi c_{cl,free} \quad (66)$$

The ion transport mechanism thus depends on the interactions between chloride ions and the cementitious matrix. The capacity of cementitious constituents to bind chloride ions is a crucial factor influencing ion transport kinetics [276]. In addition to potentially altering the cement paste's microstructure, physio-chemical reactions between chlorides and solid phases delay chloride diffusion, consequently reducing the amount of free chlorides in solution that can reach the reinforcements. The fixation isotherm refers to the relationship between the concentration of chloride ions fixed within the cement matrix and the surrounding pore solution. It describes the equilibrium state at which these ions are chemically bound or immobilized within the hydration products, specifically highlighting the retention capacity of the hydrated phases as a function of concentration during the hydration process.

VI.2- Distinction Between Apparent and Effective Diffusion Coefficients

For chloride ion diffusion, the diffusion coefficient is essential for understanding the time-dependent penetration of chlorides and predicting the service life of structures exposed to chloride environments.

There are two diffusion coefficients, both expressed in m²/s:

- **Effective Diffusion Coefficient:** This coefficient pertains to the diffusion of an ionic species within the interstitial solution of a porous cementitious material. Defined by Fick's first law, it is determined under steady-state conditions either through natural diffusion tests ($D_{ss(diff)}$ or $D_{e(diff)}$) (Luping & Nilsson, [277]) or migration tests ($D_{ss(mig)}$ or $D_{e(mig)}$) (Luping & Nilsson, 1993b [276], ASTM C1202-12 [278]).
- **Apparent Diffusion Coefficient:** This coefficient is obtained under non steady-state conditions and is defined by Fick's second law. It is measured using migration tests ($D_{nss(mig)}$ or $D_{a(mig)}$ or D_{RCM}) by assessing the depth of chloride ion penetration into concrete (NT BUILD 443 [279], 1995; NT BUILD 492 [280]; XP P 18-462, 2012). The apparent diffusion coefficient reflects the physical and chemical interactions between chlorides and the cementitious matrix. Additionally, it can be determined through diffusion tests ($D_{nss(diff)}$ or $D_{a(diff)}$) by fitting the experimentally obtained chloride profiles to the analytical solution of Fick's second law (Baroghel-Bouny et al. [281]; Ben Fraj et al. [52], ASTM C1556-11a [282]).

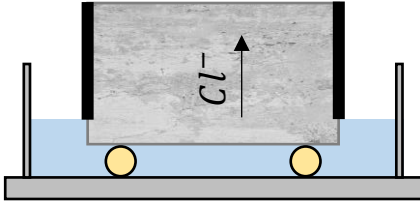
To comprehensively understand the distinctions between these diffusion coefficients, Table 22 illustrates a detailed comparison of the corresponding experimental methodologies.

Experimental methods to determine the diffusion coefficient

Natural Diffusion test

Immersion test (non-steady)

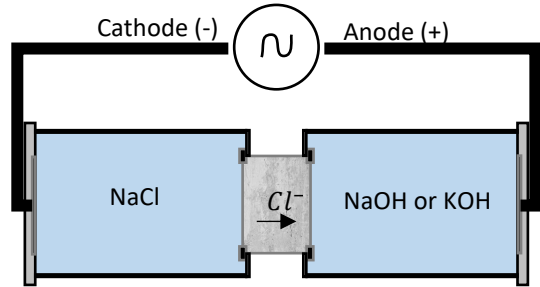
$$D_{a(diff)}$$



Migration tests

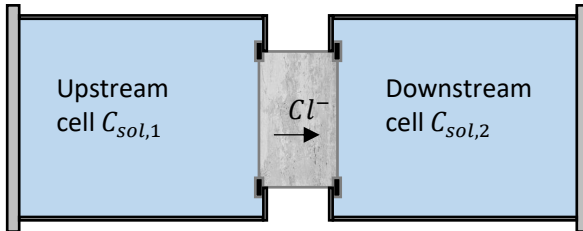
Steady state migration test

$$D_{ss(mig)} \text{ or } D_{e(mig)}$$



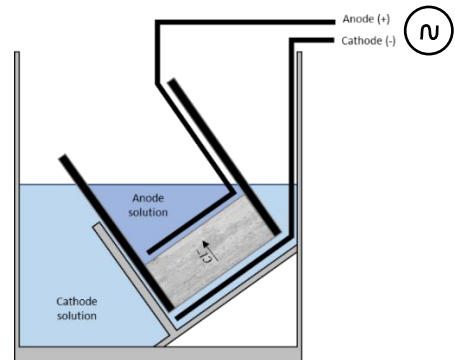
Diffusion cell (steady state)

$$D_{eff} \text{ ou } D_{e(dif)}$$

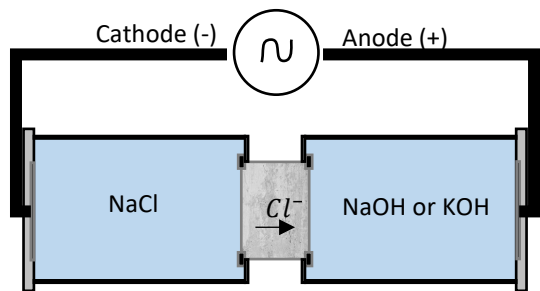


Non steady migration test

$$D_{RCM} :$$



$$D_{nss(mig)} \text{ or } D_{a(mig)} :$$



Electrical conductivity test

(To note that the effective and apparent coefficient can be related using the chloride binding isotherms)

Table 22: Experimental methods to determine various diffusion coefficients of cementitious materials.

VI.3- Modeling of Ionic Diffusion Mechanisms in Cementitious Materials

The diffusion of chloride ions into concrete is a complex process influenced by various factors. When the chloride ion concentration outside the concrete exceeds that within, a concentration gradient drives their diffusion into the material. This diffusion phenomenon is classically described by Fick's phenomenological model, which, in its simplest form, neglects chemical reactions. According to Fick's first law in steady-state conditions, the mass flux $J_{Cl,free}$ [mol.m⁻².s⁻¹], representing the quantity of ions traversing a unit area per second, is given by

$$J_{Cl,free} = -D_{eff} \frac{\partial c_{Cl,free}}{\partial x} \quad (67)$$

where D_{eff} is the effective diffusion coefficient [m².s⁻¹], $c_{Cl,free}$ is the quantity of free chlorides in the interstitial solution [mol.m⁻³solution] and x is the position [m].

Considering mass conservation, Fick's second law in non-steady-state conditions is expressed as:

$$\frac{\partial c_{Cl,tot}}{\partial t} = \frac{\partial J_{Cl,free}}{\partial x} \quad (68)$$

Considering equations (66), (67) and (68):

$$\frac{\partial c_{Cl,free}}{\partial t} \left(\frac{\partial c_{Cl,bound}}{\partial c_{Cl,free}} + \phi \right) = -D_{eff} \frac{\partial^2 c_{Cl,free}}{\partial x^2} \quad (69)$$

We can now deduce that:

$$\frac{\partial c_{Cl,free}}{\partial t} = - \frac{D_{eff}}{\frac{\partial c_{Cl,bound}}{\partial c_{Cl,free}} + \phi} \frac{\partial^2 c_{Cl,free}}{\partial x^2} \quad (70)$$

This equation can be expressed as:

$$\frac{\partial c_{Cl,free}}{\partial t} = -D_{app} \frac{\partial^2 c_{Cl,free}}{\partial x^2} \quad (71)$$

When D_{app} is the apparent diffusion coefficient, related to the effective diffusion coefficient by the porosity and the slope of the chloride binding isotherm:

$$D_{app} = \frac{D_{eff}}{\frac{\partial c_{Cl,bound}}{\partial c_{Cl,free}} + \phi} \quad (72)$$

However, in real-world scenarios, such as concrete subjected to drying-wetting cycles, chloride penetration rarely occurs under saturated conditions.

Furthermore, chloride penetration into concrete under natural conditions involves a complex interplay of factors, including the concrete's microstructure, influenced by the water-to-cement ratio, the use of mineral additives, and environmental conditions. Other parameters affecting chloride penetration include the chloride concentration in the contacting solution, the types of accompanying cations, and other anions, such as sulfates, present within the concrete [283].

VI.4- Diffusion Coefficients in Slag-Blended Cement: Experimental Data Compilation and Analysis

VI.4.1- Comprehensive Evaluation and classification: Diffusion Coefficient Database

To assess the predictive accuracy of the envisaged developed diffusion models, we gathered over 200 experimental measures of apparent and effective diffusion coefficients from various cement paste mixtures with slag substitution ratios (by mass) ranging from 0 to 0.71, as reported in the literature. These coefficients were categorized into tables 23 to 26 based on the type of diffusion coefficient measured: Table 24 for $D_{a(diff)}$, Table 25 for $D_{a(mig)}$, Table 26 for $D_{e(diff)}$, and Table 27 for $D_{e(mig)}$. The database includes the chemical compositions of the clinker and slag used, if provided in the references, or from previous works by the same authors on similar specimens. For future use, we define P_0 as the database of cement pastes with 0% slag substitution rate, P_λ as the database of cement pastes with slag substitution, and P_{all} for both.

Additionally, variables such as clinker and slag fineness, mixing and curing parameters as curing temperature (T_{curing} [°C]), water-to-binder ratio (w/b), slag substitution rate (λ), and curing time (t_{curing} [days] representing the hydration period at which the diffusion test was performed) are included. The experimental methods used to determine the effective and apparent diffusion coefficients are specified, along with the curing duration (t_{curing} [days]) and temperature(T_{curing} [°C]), if available. The ranges of these variables are presented in Table 23 for all types of diffusion coefficients.

Diffusion coefficient	w/b	λ	T_{curing} [°C]	t_{curing} [days]	T_{testing} [°C]	t_{testing} [days]	Diffusion coefficients [m²/s]	# of values		
$D_{\text{a(diff)}}$	Min	0.27	0	20	7	20	35	3E-13	39 $\left\{ \begin{array}{l} P_0 \\ P_{\lambda} \end{array} \right.$	36
	Max	0.7	0.7	60	420	50	450	5.1E-11		3
$D_{\text{a(mig)}}$	Min	0.3	0	20	28	20	3.3	3.7E-13	100 $\left\{ \begin{array}{l} P_0 \\ P_{\lambda} \end{array} \right.$	25
	Max	0.9	0.71	23	182	20	24	4.15E-11		75
$D_{\text{e(diff)}}$	Min	0.25	0	20	7	7	11.6	1.8E-13	82 $\left\{ \begin{array}{l} P_0 \\ P_{\lambda} \end{array} \right.$	66
	Max	0.7	0.7	60	210	60	360	9.2E-11		16
$D_{\text{e(mig)}}$	Min	0.23	0	20	58	0	0	7.7E-13	20 $\left\{ \begin{array}{l} P_0 \\ P_{\lambda} \end{array} \right.$	14
	Max	0.9	0.7	25	90	0	0	2.54E-11		6

Table 23: Parameter Ranges of the diffusion data collected in literature.

A comprehensive overview of the experimental diffusion tests is provided in section VI.2- and summarized in Table 22, while detailed information are accessible in the cited references. This thorough classification and documentation enables a rigorous assessment of diffusion models across a wide range of experimental conditions, whether in calibrating or evaluating calculated results.

Reference	Clinker						Slag						Mix and curing parameters						Testing parameters			
	C	S	A	M	$\bar{S}$	F	C	S	A	M	$\bar{S}$	F	B _{clinker} [m2/kg]	B _{slag} [m2/kg]	w/b	λ	T _{curing} [°C]	t _{curing} [days]	T _{testing} [°C]	t _{testing} [days]	Da(diff) [m²/s]	Experiment
Elahi [284]	0.645	0.205	0.061	0.017	0.030	0.028	0.412	0.358	0.140	0.082	0.000	0.0025	322	600	0.3	0	20	44		35	3.1E-12	Immersion test
	0.645	0.205	0.061	0.017	0.030	0.028	0.412	0.358	0.140	0.082	0.000	0.0025	322	600	0.3	0.5	20	44		35	9.8E-13	
	0.645	0.205	0.061	0.017	0.030	0.028	0.412	0.358	0.140	0.082	0.000	0.0025	322	600	0.3	0.7	20	44		35	7.3E-13	
Dousti [285]	0.633	0.224	0.047	0.036	0.017	0.037							290		0.4	0	23	150	22	450	3.13E-12	Immersion test
	0.633	0.224	0.047	0.036	0.017	0.037							290		0.4	0	23	150	35	450	4.31E-12	
	0.633	0.224	0.047	0.036	0.017	0.037							290		0.4	0	23	150	50	450	7.97E-12	
Frederiksen [286]	0.661	0.238	0.031	0.007	0.021	0.025							359		0.7	0	23	28	22	35	3.27E-11	Immersion test
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.6	0	23	28	22.5	35	2.86E-11	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.5	0	23	28	22.6	35	1.58E-11	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.45	0	23	28	22.8	35	1.36E-11	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.4	0	23	28	22.8	35	1.06E-11	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.35	0	23	28	22.9	35	7.3E-12	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.3	0	23	28	23	35	5.6E-12	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.7	0	23	28	22	35	3.83E-11	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.6	0	23	28	22.5	35	2.8E-11	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.5	0	23	28	22.6	35	1.65E-11	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.45	0	23	28	22.8	35	1.19E-11	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.4	0	23	28	22.8	35	1.03E-11	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.35	0	23	28	22.9	35	7E-12	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.3	0	23	28	23	35	4.7E-12	
Ziehensack [287]	0.628	0.200	0.056	0.014	0.040	0.029									0.5	0	20	60	20	360	8.07E-12	calculated from diffusion cell test
	0.628	0.200	0.056	0.014	0.040	0.029	0.459	0.301	0.085	0.064	0.025	0.01			0.5	0.7	20	60	20	360	3E-13	
Princigallo [288]	0.640	0.210	0.050	0.020	0.033	0.030									0.33	0	60	7	23	420	5.2051E-12	Immersion test
	0.640	0.210	0.050	0.020	0.033	0.030									0.33	0	60	21	23	420	2.9074E-12	
	0.640	0.210	0.050	0.020	0.033	0.030									0.33	0	60	50	23	420	2.0927E-12	
	0.640	0.210	0.050	0.020	0.033	0.030									0.33	0	60	140	23	420	1.8772E-12	
	0.640	0.210	0.050	0.020	0.033	0.030									0.33	0	60	420	23	420	1.4896E-12	
	0.640	0.210	0.050	0.020	0.033	0.030									0.3	0	60	7	23	420	3.4461E-12	
	0.640	0.210	0.050	0.020	0.033	0.030									0.3	0	60	21	23	420	2.3789E-12	
	0.640	0.210	0.050	0.020	0.033	0.030									0.3	0	60	50	23	420	1.9302E-12	
	0.640	0.210	0.050	0.020	0.033	0.030									0.3	0	60	140	23	420	1.5705E-12	
	0.640	0.210	0.050	0.020	0.033	0.030									0.3	0	60	420	23	420	1.3663E-12	
	0.640	0.210	0.050	0.020	0.033	0.030									0.27	0	60	7	23	420	2.0752E-12	
	0.640	0.210	0.050	0.020	0.033	0.030									0.27	0	60	21	23	420	1.4527E-12	
	0.640	0.210	0.050	0.020	0.033	0.030									0.27	0	60	50	23	420	2.081E-12	
	0.640	0.210	0.050	0.020	0.033	0.030									0.27	0	60	140	23	420	1.0283E-12	
	0.640	0.210	0.050	0.020	0.033	0.030									0.27	0	60	420	23	420	9.4054E-13	
Numata [289]															0.55	0	25	28	23	126	3.80E-11	immersion test
															0.4	0	25	28	23	126	5.10E-11	

Table 24: Material compositions and conditions of the diffusion database for $D_{a(diff)}$.

Reference	Clinker						Slag						Mix and curing parameters						Testing parameters			
	C	S	A	M	$\bar{S}$	F	C	S	A	M	$\bar{S}$	F	B _{clinker} [m2/kg]	B _{slag} [m2/kg]	w/b	λ	T _{curing} [°C]	t _{curing} [days]	T _{testing} [°C]	t _{testing} [days]	Da(mig) [m²/s]	Experiment
Frederiksen [286]	0.661	0.238	0.031	0.007	0.021	0.025							359		0.7	0	23	28	20	3.3	3.9E-11	Migration test nss
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.6	0	23	28	20	6	3.41E-11	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.5	0	23	28	20	11	1.93E-11	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.45	0	23	28	20	12.25	1.8E-11	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.4	0	23	28	20	16	1.49E-11	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.35	0	23	28	20	17	1.1E-11	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.3	0	23	28	20	24	7.83E-12	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.7	0	23	28	20	3.3	4.15E-11	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.6	0	23	28	20	6	3.27E-11	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.5	0	23	28	20	11	1.78E-11	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.45	0	23	28	20	12.25	1.74E-11	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.4	0	23	28	20	16	1.38E-11	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.35	0	23	28	20	17	1.1E-11	
	0.661	0.238	0.031	0.007	0.021	0.025							359		0.3	0	23	28	20	24	7.83E-12	
Van Noort [290]															0.45	0.66	20	28		24	5.78E-12	Migration test nss
															0.45	0.66	20	28		24	5.76E-12	
															0.45	0.66	20	28		24	5.28E-12	
															0.45	0.66	20	28		24	4.34E-12	
															0.45	0.66	20	28		24	4.96E-12	
															0.45	0.66	20	28		24	4.14E-12	
															0.45	0.66	20	28		24	3.56E-12	
															0.45	0.66	20	28		24	3.67E-12	
															0.45	0.66	20	28		24	3.45E-12	
															0.45	0.66	20	28		24	6.64E-12	
															0.4	0.66	20	28		24	5.01E-12	
															0.55	0.66	20	28		24	6.22E-12	
															0.55	0.66	20	28		24	5.86E-12	
															0.4	0.66	20	28		24	4.31E-12	
															0.55	0.66	20	28		24	5.81E-12	
															0.47	0.66	20	28		24	4.71E-12	
															0.47	0.66	20	28		24	4.11E-12	
															0.4	0.66	20	28		24	3.75E-12	
															0.45	0.66	20	28		24	3.36E-12	
															0.4	0.66	20	28		24	1.33E-12	
															0.55	0.66	20	28		24	2.76E-12	
															0.55	0.66	20	28		24	1.86E-12	
															0.4	0.66	20	28		24	1.22E-12	
															0.55	0.66	20	28		24	1.56E-12	
															0.45	0.66	20	28		24	1.47E-12	
															0.47	0.66	20	28		24	1.23E-12	
															0.47	0.66	20	28		24	1.34E-12	

						0.4	0.66	20	28	24	1.19E-12	
						0.45	0.66	20	28	24	1.14E-12	
						0.45	0.7	20	28	24	3.21E-12	
						0.4	0.7	20	28	24	2.05E-12	
						0.55	0.7	20	28	24	2.96E-12	
						0.55	0.7	20	28	24	3.48E-12	
						0.4	0.7	20	28	24	2.02E-12	
						0.55	0.7	20	28	24	2.72E-12	
						0.47	0.7	20	28	24	2.19E-12	
						0.47	0.7	20	28	24	2.44E-12	
						0.4	0.7	20	28	24	1.43E-12	
						0.45	0.7	20	28	24	2.09E-12	
						0.45	0.71	20	28	24	1.62E-12	
						0.45	0.64	20	28	24	5.78E-12	
						0.45	0.64	20	28	24	2.95E-12	
						0.45	0.65	20	28	24	3.08E-12	
						0.45	0.67	20	28	24	3.89E-12	
						0.45	0.67	20	28	24	2.03E-12	
						0.45	0.66	20	28	24	3.73E-12	
						0.45	0.66	20	28	24	2.66E-12	
						0.45	0.66	20	182	24	1.52E-12	
						0.45	0.66	20	182	24	1.45E-12	
						0.45	0.66	20	182	24	1.7E-12	
						0.45	0.66	20	182	24	1.64E-12	
						0.45	0.66	20	182	24	1.74E-12	
						0.45	0.66	20	182	24	1.66E-12	
						0.45	0.66	20	182	24	1.76E-12	
						0.4	0.66	20	182	24	1.04E-12	
						0.55	0.66	20	182	24	1.79E-12	
						0.55	0.66	20	182	24	1.79E-12	
						0.4	0.66	20	182	24	1.76E-12	
						0.55	0.66	20	182	24	1.95E-12	
						0.47	0.66	20	182	24	1.48E-12	
						0.47	0.66	20	182	24	1.51E-12	
						0.4	0.66	20	182	24	1.52E-12	
						0.45	0.66	20	182	24	3.7E-13	
						0.45	0.7	20	182	24	1.38E-12	
						0.4	0.7	20	182	24	1.66E-12	
						0.55	0.7	20	182	24	1.75E-12	
						0.55	0.7	20	182	24	1.91E-12	
						0.4	0.7	20	182	24	1.4E-12	
						0.55	0.7	20	182	24	1.55E-12	
						0.47	0.7	20	182	24	1.12E-12	
						0.4	0	22	90	>30	2.9E-12	Accelerated chloride penetration test
						0.6	0	22	90	>30	9.4E-12	

Luping & Nilsson [276]	0.621	0.199	0.053	0.013	0.03	0.028	0.8	0	22	90	>30	2.1E-11
	0.621	0.199	0.053	0.013	0.03	0.028	0.4	0	22	90	>30	2.9E-12
	0.621	0.199	0.053	0.013	0.03	0.028	0.6	0	22	90	>30	9.4E-12
	0.621	0.199	0.053	0.013	0.03	0.028	0.5	0	22	90	>30	5.8E-12
	0.621	0.199	0.053	0.013	0.03	0.028	0.7	0	22	90	>30	9.3E-12
	0.621	0.199	0.053	0.013	0.03	0.028	0.9	0	22	90	>30	1.91E-11
	0.621	0.199	0.053	0.013	0.03	0.028	0.5	0	22	90	>31	5.80E-12
	0.621	0.199	0.053	0.013	0.03	0.028	0.7	0	22	90	>32	9.30E-12
	0.621	0.199	0.053	0.013	0.03	0.028	0.9	0	22	90	>33	1.91E-11

Table 25: Material compositions and conditions of the diffusion database for $D_{a(mig)}$.

Reference	Clinker						Slag						Mix and curing parameters						Testing parameters			
	C	S	A	M	$\bar{S}$	F	C	S	A	M	$\bar{S}$	F	B _{clinker} [m2/kg]	B _{slag} [m2/kg]	w/b	λ	T _{curing} [°C]	t _{curing} [days]	T _{testing} [°C]	t _{testing} [days]	De(diff) [m²/s]	Experiment
Ziehensack [287]	0.627	0.199	0.055	0.014	0.039	0.028									0.5	0	20	60	20	360	2.94E-12	Diffusion cell
	0.627	0.199	0.055	0.014	0.039	0.028	0.459	0.301	0.084	0.064	0.025	0.0104			0.5	0.7	20	60	20	360	1.8E-13	
Page [291]	0.63	0.203	0.071	0.013	0.033	0.027									0.4	0	22	60	7	21	1.103E-12	Diffusion cell
	0.63	0.203	0.071	0.013	0.033	0.027									0.4	0	22	60	14.5	21	1.27E-12	
	0.63	0.203	0.071	0.013	0.033	0.027									0.4	0	22	60	25	21	2.6E-12	
	0.63	0.203	0.071	0.013	0.033	0.027									0.4	0	22	60	35	21	4.47E-12	
	0.63	0.203	0.071	0.013	0.033	0.027									0.4	0	22	60	44	21	8.4E-12	
	0.63	0.203	0.071	0.013	0.033	0.027									0.5	0	22	60	7	21	2.07E-12	
	0.63	0.203	0.071	0.013	0.033	0.027									0.5	0	22	60	13.5	21	2.36E-12	
	0.63	0.203	0.071	0.013	0.033	0.027									0.5	0	22	60	25	21	4.47E-12	
	0.63	0.203	0.071	0.013	0.033	0.027									0.5	0	22	60	33.5	21	9.48E-12	
	0.63	0.203	0.071	0.013	0.033	0.027									0.5	0	22	60	45	21	1.836E-11	
	0.63	0.203	0.071	0.013	0.033	0.027									0.6	0	22	60	7	21	5.19E-12	
	0.63	0.203	0.071	0.013	0.033	0.027									0.6	0	22	60	14.5	21	8.46E-12	
	0.63	0.203	0.071	0.013	0.033	0.027									0.6	0	22	60	25	21	1.235E-11	
	0.63	0.203	0.071	0.013	0.033	0.027									0.6	0	22	60	35	21	1.652E-11	
	0.63	0.203	0.071	0.013	0.033	0.027									0.6	0	22	60	47	21	3.182E-11	
	0.63	0.203	0.071	0.013	0.033	0.027	0.423	0.333	0.107	0.087	0	0.0033			0.5	0.65	22	60	25	21	4.10E-13	
Ngala [292]	0.635	0.212	0.053	0.013	0.033	0.026									0.4	0	38	84	25	21	3.95E-12	Diffusion cell
	0.635	0.212	0.053	0.013	0.033	0.026									0.5	0	38	84	25	21	7.8E-12	
	0.635	0.212	0.053	0.013	0.033	0.026									0.6	0	38	84	25	21	1.26E-11	
	0.635	0.212	0.053	0.013	0.033	0.026									0.7	0	38	84	25	21	2.146E-11	
Ngala & Page [293]	0.635	0.212	0.053	0.013	0.033	0.026	0.400	0.355	0.125	0.091	0.001	0.0058			0.4	0.65	38	84	25	21	2.6495E-13	Diffusion cell
	0.635	0.212	0.053	0.013	0.033	0.026	0.400	0.355	0.125	0.091	0.001	0.0058			0.5	0.65	38	84	25	21	3.4065E-13	
	0.635	0.212	0.053	0.013	0.033	0.026	0.400	0.355	0.125	0.091	0.001	0.0058			0.6	0.65	38	84	25	21	5.299E-13	
	0.635	0.212	0.053	0.013	0.033	0.026	0.400	0.355	0.125	0.091	0.001	0.0058			0.7	0.65	38	84	25	21	8.9326E-13	
MacDonald et Northwood [294]															0.4	0	23	56	25	21	2.5659E-12	Diffusion cell
															0.5	0	23	56	25	21	6.9494E-12	
															0.6	0	23	56	25	21	1.3108E-11	
															0.7	0	23	56	25	21	2.0656E-11	
Castellote [295]	0.628	0.193	0.061	0.017	0.032	0.031									0.4	0	25	58			3.67E-12	Diffusion cell
Hornain [296]	0.654	0.211	0.050	0.007	0.033	0.026							380		0.55	0	20	62	20	120	1.125E-11	Diffusion cell
Caré [297]	0.672	0.215	0.053	0.02	0.03	0.03							320		0.45	0	45	30		40	5.65E-12	Calculated from immersion test
Huang [298]															0.4	0	38	28	25	14	5.42E-12	Diffusion cell
															0.5	0	38	28	25	14	8.24E-12	
															0.6	0	38	28	25	14	1.20E-11	
Fleury [299]															0.4	0	20	180		11.6	1.80E-12	Calculated
															0.4	0	20	180		11.6	2.00E-12	
															0.4	0	20	180		11.6	2.50E-12	
Larbi [300]	0.666	0.224	0.029	0.009	0.021	0.023									0.4	0	20	92	20		2.55E-12	diffusion cell test

Wilson [301]	0.65	0.207	0.054	0.011	0.029	0.019				0.3	0	20	28		21	1.03E-12	diffusion cell test (mini-migration test)
	0.65	0.207	0.054	0.011	0.029	0.019				0.4	0	20	28		21	1.16E-12	
	0.65	0.207	0.054	0.011	0.029	0.019				0.5	0	20	28		21	2.16E-12	
	0.65	0.207	0.054	0.011	0.029	0.019				0.4	0	20	210		21	9.22E-13	
	0.65	0.207	0.054	0.011	0.029	0.019	0.408	0.343	0.09	0.075	0.055	0.005	28		21	2.93E-13	
	0.65	0.207	0.054	0.011	0.029	0.019	0.408	0.343	0.09	0.075	0.055	0.005	28		21	4.68E-13	
	0.65	0.207	0.054	0.011	0.029	0.019	0.408	0.343	0.09	0.075	0.055	0.005	28		21	4.89E-13	
	0.65	0.207	0.054	0.011	0.029	0.019	0.408	0.343	0.09	0.075	0.055	0.005	210		21	2.69E-13	
Johnston [302]										0.35	0	20	56		21	7.19E-12	diffusion cell
										0.25	0	20	56		21	5.18E-12	
Kumar [303]	0.648	0.202	0.039	0.045	0.024	0.034				550	0.4	0	27	7	27	1.13E-11	diffusion cell
	0.648	0.202	0.039	0.045	0.024	0.034				550	0.4	0	38	7	38	9.08E-12	
	0.648	0.202	0.039	0.045	0.024	0.034				550	0.4	0	60	7	60	2.00E-11	
	0.648	0.202	0.039	0.045	0.024	0.034				550	0.4	0	27	28	27	8.84E-12	
	0.648	0.202	0.039	0.045	0.024	0.034				550	0.4	0	38	28	38	2.27E-11	
	0.648	0.202	0.039	0.045	0.024	0.034				550	0.4	0	60	28	60	3.32E-11	
	0.648	0.202	0.039	0.045	0.024	0.034				550	0.35	0	27	7	27	8.82E-12	
	0.648	0.202	0.039	0.045	0.024	0.034				550	0.35	0	38	7	38	6.89E-12	
	0.648	0.202	0.039	0.045	0.024	0.034				550	0.35	0	60	7	60	1.43E-11	
	0.648	0.202	0.039	0.045	0.024	0.034				550	0.35	0	27	28	27	7.51E-12	
	0.648	0.202	0.039	0.045	0.024	0.034				550	0.35	0	38	28	38	1.38E-11	
	0.648	0.202	0.039	0.045	0.024	0.034				550	0.35	0	60	28	60	2.15E-11	
	0.648	0.202	0.039	0.045	0.024	0.034	0.420	0.327	0.1	0.11	0.001	0.0086	27	7	27	2.79E-12	
	0.648	0.202	0.039	0.045	0.024	0.034	0.420	0.327	0.1	0.11	0.001	0.0086	38	7	38	4.30E-12	
	0.648	0.202	0.039	0.045	0.024	0.034	0.420	0.327	0.1	0.11	0.001	0.0086	60	7	60	5.52E-12	
	0.648	0.202	0.039	0.045	0.024	0.034	0.420	0.327	0.1	0.11	0.001	0.0086	27	28	27	5.14E-13	
	0.648	0.202	0.039	0.045	0.024	0.034	0.420	0.327	0.1	0.11	0.001	0.0086	38	28	38	7.46E-13	
	0.648	0.202	0.039	0.045	0.024	0.034	0.420	0.327	0.1	0.11	0.001	0.0086	60	28	60	2.50E-12	
Chatterji [304]										0.4	0	22	7	25	30	2.46E-12	diffusion cell
										0.4	0	22	7	25	30	5.40E-12	
Chatterji [305]										0.4	0	22	7	25		8.20E-12	diffusion cell
Goto [306]	0.628	0.208	0.052	0.032	0.028	0.029				0.4	0	27	28	27		6.90E-12	diffusion cell
	0.647	0.217	0.037	0.032	0.016	0.039				0.3	0	27	7	27		2.70E-11	
	0.647	0.217	0.037	0.032	0.016	0.039				0.3	0	27	28	27		8.50E-12	
	0.628	0.208	0.052	0.032	0.028	0.029				0.4	0	60	28	60		9.20E-11	
	0.628	0.208	0.052	0.032	0.028	0.029				0.4	0	60	28	45		3.70E-11	
	0.628	0.208	0.052	0.032	0.028	0.029				0.4	0	60	42	45		3.70E-11	
	0.628	0.208	0.052	0.032	0.028	0.029				0.4	0	60	28	35		2.70E-11	
	0.628	0.208	0.052	0.032	0.028	0.029				0.4	0	60	42	35		3.70E-11	
Yu [307]	0.63	0.203	0.071	0.013	0.033	0.027				0.35	0	25	90			1E-12	diffusion cell
	0.63	0.203	0.071	0.013	0.033	0.027				0.5	0	25	90			5.45E-12	
	0.63	0.203	0.071	0.013	0.033	0.027				0.6	0	25	90			7.28E-12	
	0.63	0.203	0.071	0.013	0.033	0.027				0.6	0	25	90			7.28E-12	

Table 26: Material compositions and conditions of the diffusion database for $D_{e(diff)}$.

Reference	Clinker						Slag						Mix and curing parameters						Testing parameters			
	C	S	A	M	$\bar{S}$	F	C	S	A	M	$\bar{S}$	F	$B_{clinker}$ [m2/kg]	B_{slag} [m2/kg]	w/b	λ	T_{curing} [°C]	t_{curing} [days]	$T_{testing}$ [°C]	$t_{testing}$ [days]	$De(mig)$ [m ² /s]	Experiment
McNally & Sheils [308]	0.628	0.198	0.048	0.019	0.0	0.031							320	400	0.55	0	20	90			1.42E-11	calculated from Migration nss test
	0.628	0.198	0.048	0.019	0.0	0.031	0.398	0.361	0.121	0.069	0.0	0.0	320	400	0.55	0.5	20	90			1.3E-12	
	0.628	0.198	0.048	0.019	0.0	0.031	0.398	0.361	0.121	0.069	0.0	0.0	320	400	0.55	0.7	20	90			7.7E-13	
	0.628	0.198	0.048	0.019	0.0	0.031	0.398	0.361	0.121	0.069	0.0	0.0	320	400	0.55	0.7	20	90			8.1E-13	
	0.628	0.198	0.048	0.019	0.0	0.031	0.398	0.361	0.121	0.069	0.0	0.0	320	400	0.45	0	20	90			7.01E-12	
	0.628	0.198	0.048	0.019	0.0	0.031	0.398	0.361	0.121	0.069	0.0	0.0	320	400	0.45	0.5	20	90			8.1E-13	
	0.628	0.198	0.048	0.019	0.0	0.031	0.398	0.361	0.121	0.069	0.0	0.0	320	400	0.45	0.7	20	90			1E-12	
	0.628	0.198	0.048	0.019	0.0	0.031	0.398	0.361	0.121	0.069	0.0	0.0	320	400	0.45	0.7	20	90			1.07E-12	
Luping & Nilsson [276]	0.621	0.199	0.053	0.013	0.03	0.028									0.4	0	22	90		>30	9.3E-12	Calculated from Accelerated chloride penetration test
	0.621	0.199	0.053	0.013	0.03	0.028									0.6	0	22	90		>30	1.75E-11	
	0.621	0.199	0.053	0.013	0.03	0.028									0.8	0	22	90		>30	2.54E-11	
	0.621	0.199	0.053	0.013	0.03	0.028									0.4	0	22	90		>30	7.2E-12	
	0.621	0.199	0.053	0.013	0.03	0.028									0.6	0	22	90		>30	1.56E-11	
	0.621	0.199	0.053	0.013	0.03	0.028									0.5	0	22	90		>30	5.8E-12	
	0.621	0.199	0.053	0.013	0.03	0.028									0.7	0	22	90		>30	9.3E-12	
	0.621	0.199	0.053	0.013	0.03	0.028									0.9	0	22	90		>30	1.91E-11	
Castellote [295]	0.628	0.193	0.061	0.017	0.032	0.031									0.4	0	25	58			3.87E-12	Calculated from diffusion cell test
Sun [309]	0.624	0.213	0.046	0.030	0.022	0.033									0.23	0	20				1.03E-12	Migration ss test
	0.624	0.213	0.046	0.030	0.022	0.033									0.35	0	20	long period /end of hydration			4.12E-12	
	0.624	0.213	0.046	0.030	0.022	0.331									0.53	0	20				1.06E-11	

Table 27: Material compositions and conditions of the diffusion database for $D_{e(mig)}$.

VI.4.2- Diffusion Coefficients Database Analysis

The diffusion coefficients gathered in Table 24-Table 27 has been thoroughly analyzed to assess the influence of various parameters (chemical composition of clinker and slag, their fineness, T_{curing} , water-to-binder ratio (w/b), slag substitution rate (λ), and curing time t_{curing}). Only the analysis of the effective diffusion coefficient database is presented here, as the evaluations of both the apparent and effective diffusion coefficients yielded identical results. Given that the effective diffusion coefficient will be used in the subsequent multi-scale model, we have focused exclusively on its corresponding databases for further analysis.

Figure 70 illustrates the effective diffusion coefficient D_{eff} as a function of curing time, alongside the temperatures at which the samples were cured. For curing durations less than 100 days ($t_{\text{curing}} < 100$ days), there is significant dispersion in D_{eff} . This suggests that an accurate prediction of the diffusion coefficient necessitates consideration of multiple parameters. Additionally, discrepancies may arise from how the experiments are conducted or how the results are interpreted. The observed discrepancies indicate that for same curing time, D_{eff} can vary among samples with different water-to-binder ratios, slag substitution rates, and chemical compositions... This variability suggests that the input parameters documented in the dataset and which are mainly related to the formulation of materials may significantly contribute to these differences, and thus needed to be taken into consideration when developing an accurate diffusion model.

Moreover, the data reveals that within the same time range ($t_{\text{curing}} < 100$ days), samples cured at higher temperatures generally exhibit higher diffusion coefficients compared to those cured at lower temperatures. This temperature effect is typically accounted for using Arrhenius-type equations in the literature. To mitigate this temperature effect, this study retains only data points from samples cured at room temperature (between 20°C and 25°C) for subsequent analysis.

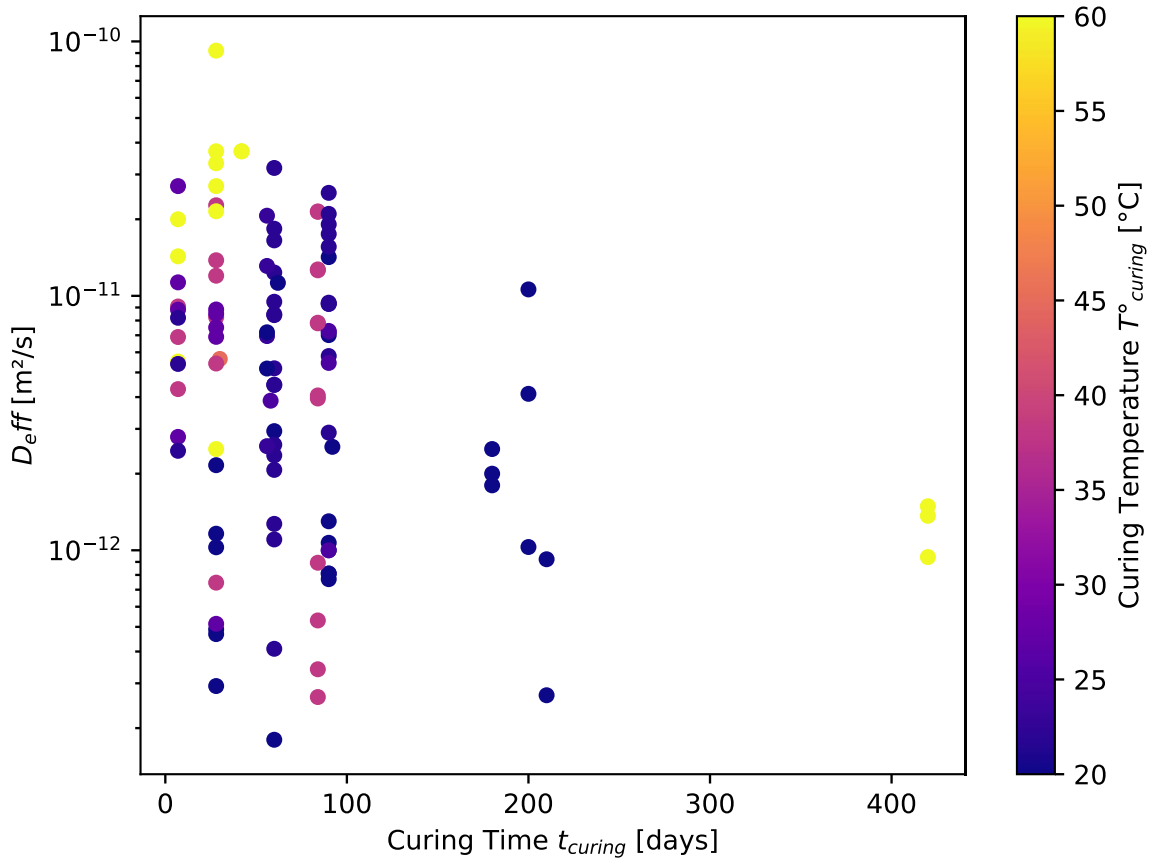


Figure 70: Distribution of effective diffusion coefficients as a function of curing time.

Focusing exclusively on the diffusion coefficient for samples tested at room temperature ($20^{\circ}\text{C} < T_{\text{curing}} < 25^{\circ}\text{C}$), Figure 71 illustrates the distribution of the effective diffusion coefficient D_{eff} as a function of the initial water-to-binder ratio (w/b), with the slag substitution rate color-coded to highlight its impact. A critical observation from this figure is that as the w/b ratio increases, the diffusion coefficient also increases. This phenomenon can be logically attributed to the expansion of the porosity network due to the higher initial water content.

Although this trend is evident, discrepancies exist between data points, even for similar w/b ratios and slag substitution rates. This indicates that, while the w/b ratio and slag substitution significantly influence the diffusion coefficient, additional factors must also be considered (e.g, the curing time).

Notably, data points for samples with slag substitution consistently exhibit lower diffusion coefficients compared to those without slag substitution at the same w/b ratios. This supports our initial hypothesis that substituting cement with slag enhances the diffusion coefficient, reflecting the beneficial effects of slag substitution on the microstructural properties of the cementitious matrix.

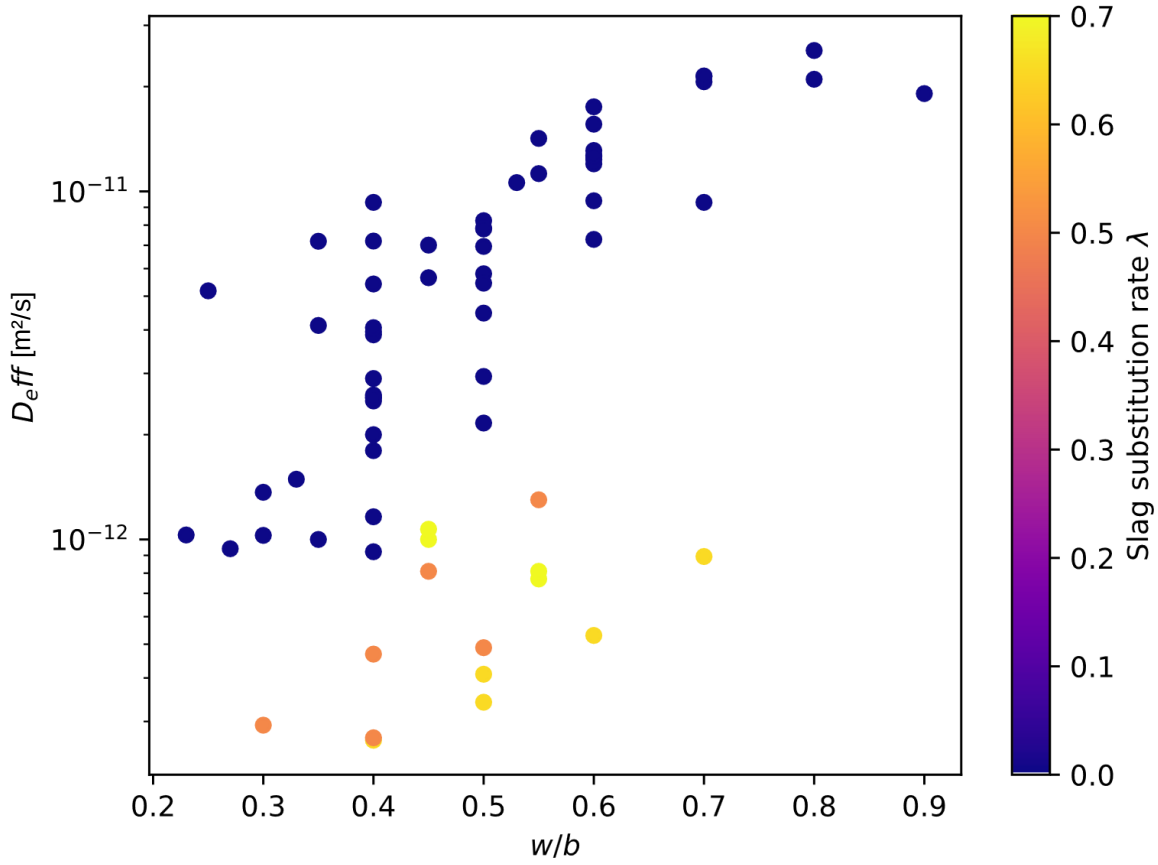


Figure 71: Distribution of effective diffusion coefficients as a function of water over binder ratio.

To investigate the effect of slag substitution on the diffusion coefficient, a dedicated analysis is carried out. This analysis compares D_{eff} from the experimental database (Table 26 and Table 27, 103 data points) to porosities calculated for the same database using the full hydration model developed in Chapter IV (see Figure 72). This indicates that the reduction in the effective diffusion coefficient due to slag addition cannot be solely explained by total porosity, as it remains similar to that of OPC pastes for a given water-to-cement ratio.

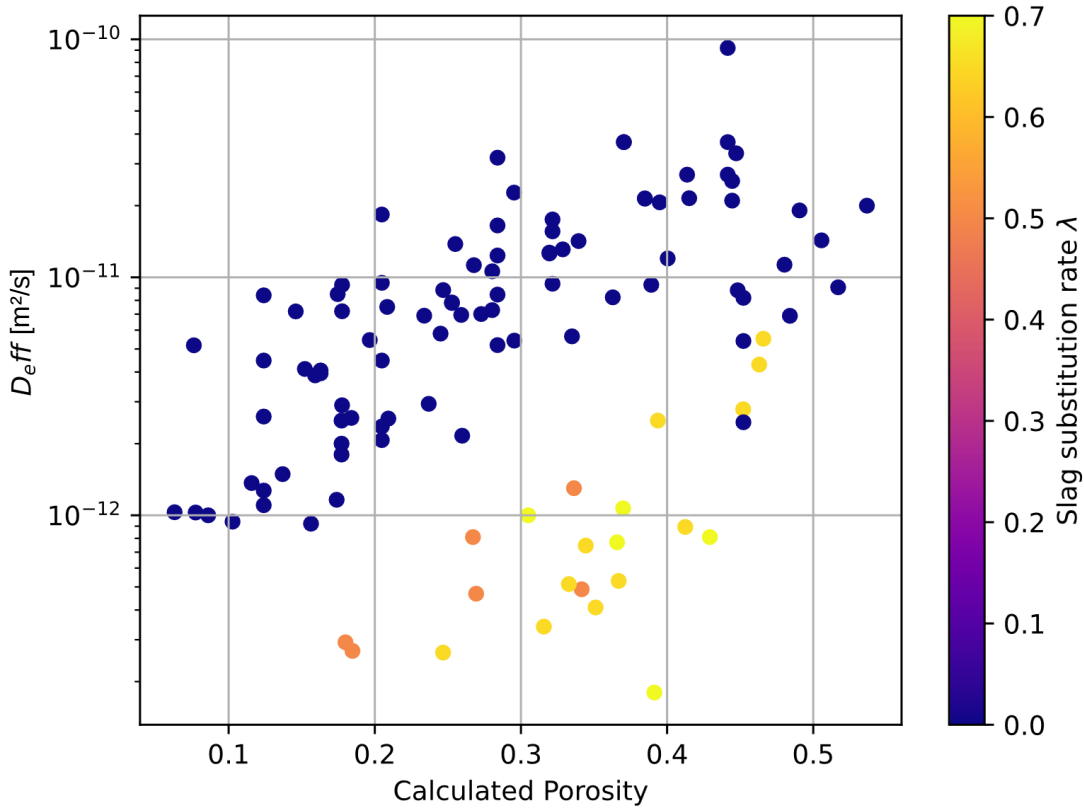


Figure 72: Distribution of the effective diffusion coefficient of the database (Table 26 and Table 27) in function of the calculated porosities from the hydration model of Chapter IV and slag substitution rate.

A critical observation from Figure 72 is the absence of relationship between porosity and the diffusion coefficient, if the slag substitution is ignored. In turn, for a given slag substitution rate, there is an increasing trend of D_{eff} with porosity. This trend is logically attributed to the expansion of the pore network, driven by the higher initial water content. Despite this clear trend, discrepancies exist among data points with similar porosities and slag substitution rates, indicating the influence of additional factors.

Notably, samples with slag substitution consistently show lower diffusion coefficients compared to those without slag substitution, even at the same porosity levels. This conclusion supports literature findings incorporating slag in cement reduce the diffusion coefficient.

VI.5- Conclusion

The diffusion properties of slag-blended cements have been thoroughly examined in this chapter. A comprehensive database of D_{eff} and D_{app} values from the literature has been compiled and analyzed, yielding several key insights:

- There is no clear, direct relationship between porosity and the diffusion coefficient for both OPC and slag-blended cements. This highlights the necessity of developing a model that integrates porosity characteristics to more accurately determine the diffusion coefficient.
- Samples with slag substitution consistently demonstrate lower diffusion coefficients compared to those without slag, even at equivalent porosity levels.
- Accurate prediction of the diffusion coefficient requires consideration of multiple parameters (w/b, temperature, curing time, slag substitution rate...), that should be taken into consideration when developing a multi-scale diffusion model.
- Samples cured at higher temperatures tend to exhibit higher diffusion coefficients compared to those cured at lower temperatures. This highlights the necessity of integrating the developed hydration model in the developing of the diffusion model, as it incorporates temperature as an input parameter influencing the kinetics of both cement and slag hydration.
- As the water-to-binder ratio (w/b) increases, the diffusion coefficient generally increases. However, notable discrepancies exist, even for samples with similar w/b ratios and slag substitution levels.

These findings, in combination with the microstructural observations from Chapter V, will be integrated with the hydration model developed in Chapter IV to create a comprehensive multi-scale diffusion model for slag-blended cements.

Chapter VII

Multi-Scale Modeling Of Diffusion Properties Of Cementitious Materials

In concrete, cement paste is the phase that predominantly governs the mechanical and diffusive properties of concrete at early ages and in the long term [10, 190]. It is a that matrix binds the concrete constituents and evolves over time. During hydration, the microstructure of cement paste evolves with the formation of hydration products such as calcium silicates (C-S-H) or portlandite crystals, and the development of the porous network. On one hand, the hydrates form a solid phase that increasingly percolates to impart strength and stiffness to the cement paste. On the other hand, the connectivity of the porous network decreases significantly during hydration, affecting the penetration rate of chloride ions.

Various models have been developed to relate the diffusion properties of cement paste to its microstructure, encompassing empirical, multi-scale, and numerical approaches. Empirical models can establish law relationships (such as power laws) between diffusivity, porosity, temperature, and other factors, providing a practical yet specific solution limited by the experimental conditions [310]. Multi-scale models, which describe heterogeneous materials by detailing their microstructure and constituent phases, face challenges due to the complexity and varying pore sizes of cement paste [190, 311].

VII.1- Homogenization theory and techniques

Homogenization theory aims to determine the macroscopic behavior of a system that is microscopically heterogeneous. This approach allows for the modeling of various properties of heterogeneous media, such as thermal or electrical conductivity, stiffness, diffusivity, and permeability. Essentially, it involves replacing the heterogeneous material with a fictitious homogeneous one, known as the 'homogenized' material, whose properties represent an average of those of the original heterogeneous system [312]. Homogenization consists in computing the effective homogeneous properties from the microscopic description of a heterogeneous media. In essence, homogenization is a rigorous form of averaging [313, 314].

Homogenization theory has broad applications in science and technology, where boundary value problems are common [315]. The process of homogenization can be rigorously justified from multi-scale asymptotic expansion of materials with periodic microstructure whose size is much smaller than the size of fluctuation of the fields in the macroscopic structure. This process transitions from a microscopic to a macroscopic description, yielding an effective representation of the system [316, 317]. This method of asymptotic analysis and averaging is the essence of homogenization.

Importantly, homogenization is not limited to periodic structures; it can be applied to any form of heterogeneous media, accommodating various geometric configurations [318].

VII.1.1- Homogenization Schemes Based on Eshelby's Problem

In this study, multi-scale models are developed to estimate the chloride ion diffusion coefficient in slag-blended cement paste, based on the micromechanics of continuous media approach [319]. Within this

framework, homogenization schemes based on Eshelby's problem are well-established tools for estimating the effective behavior of composite materials. This section provides a brief overview of the differences among the most commonly used homogenization schemes [319–321]. The objective is to offer the technical means to transition between the different scales observed in cement pastes, which will be described in the following section. This subsequent part will focus on explaining the principles of these homogenization schemes.

Homogenization schemes allow to estimate the effective properties of heterogeneous materials by considering their microstructural characteristics. Some of the existing homogenization schemes in the literature includes Lielens method (1999) [322], asymptotic homogenization scheme RAHS (cylindrical fibers) [323], Effective self-consistent scheme (ESCS) [324]. An alternative approach involves the bounds on homogenized properties: Voigt-Reuss [325, 326], Hashin-Shtrikman [327], Gross and Seelig 2001 [328], Nemat-Nasser and Hori 1999 [329].

An important concept is the Eshelby problem [330], which addresses the elastic field inside an ellipsoidal inclusion embedded in an infinite matrix, forms the basis for many homogenization approaches. The Eshelby problem deals with a matrix having a stiffness in which there is an embedded inclusion of an ellipsoidal shape having another stiffness. By using a formal analogy between stiffness homogenization and diffusion coefficient homogenization, it is equivalently possible to define Eshelby-like problems in the context of diffusion.

The most used homogenization analytical techniques are Mori-Tanaka and self-consistent methods that are based on the Eshelby's problem [311, 331–335]. The Mori-Tanaka method is suited to matrix-inclusion composites. This approach is particularly useful for materials with moderate volume fractions of inclusions and can accommodate a variety of inclusion shapes and distributions.

Another important scheme is the self-consistent method, which treats each phase of the composite material as if it was embedded in the effective medium itself. This method is more suited for polycrystalline materials or disordered materials, in other words, which do not have a matrix phase.

The differences between the most commonly used homogenization schemes are briefly described with particular attention to the assumptions regarding the connectivity of different phases that constitute the material [336] in the next sections VII.1.1-, VII.1.2-VII.1.3-.

VII.1.1.1- Representative Elementary Volume (REV)

The micromechanical approach allows deriving the diffusion coefficients of a heterogeneous material from the definition of a representative elementary volume (REV) of its microstructure. The input parameters of the REV are the local properties of the phases constituting the heterogeneous material and their morphology. This approach relies on the principle of scale separation, which requires that the size of the

REV be much smaller than the characteristic size of the macrostructure's field fluctuations and much larger than the characteristic size of the microstructure's heterogeneity (Figure 73).

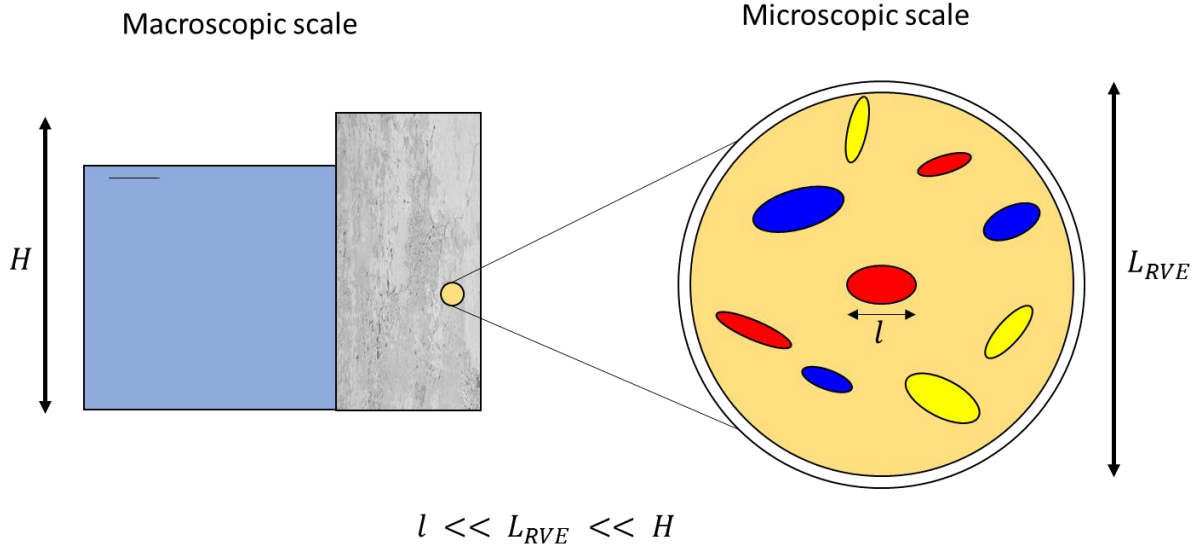


Figure 73: Homogenization theory and Representative Elementary Volume (REV) sizes.

It is essential to precisely define the homogenization problem in the domain of the REV(Ω). The field equations are:

$$\begin{cases} \text{div } j = 0 & (\Omega) \\ j(x) = -D(x) \cdot \nabla c(x) & (\Omega) \end{cases} \quad (73)$$

Subjected to one of the following boundary conditions:

- Dirichlet boundary conditions for uniform concentration gradients:

$$c = \nabla C \cdot x \quad (\partial\Omega) \quad (74)$$

- Neumann boundary conditions for uniform flux:

$$\underline{j} \cdot \underline{n} = \underline{J} \cdot \underline{n} \quad (\partial\Omega) \quad (75)$$

- Periodic boundary conditions:

$$(c - \nabla C \cdot x) \text{ periodic and } j \cdot n \text{ anti-periodic } (\partial\Omega) \quad (76)$$

$\mathbf{j}$ represents the flux vector, c is the concentration, $\mathbf{J}$ is the macroscopic flux, $\nabla \mathbf{C}$ denotes the macroscopic concentration gradient, $\mathbf{n}$ is the outward normal vector to the boundary $\partial\Omega$, and $\mathbf{D}(\mathbf{x})$ is the heterogeneous diffusion tensor field.

For the transition from the microscale to the macroscale, we apply the averaging rules:

$$\mathbf{J} = \langle \mathbf{j} \rangle \text{ and } \nabla \mathbf{C} = \langle \nabla c \rangle \quad (77)$$

where $\langle \cdot \rangle$ indicates the volume average over the REV.

By linearity of the homogenization problem, all the fields are proportional to the loading parameter. In the case of uniform concentration gradient Dirichlet boundary conditions, the microscopic concentration gradient is linearly related to the macroscopic are by:

$$\nabla c(\mathbf{x}) = \mathbf{A}(\mathbf{x}) \cdot \nabla \mathbf{C} \quad (78)$$

Where $\mathbf{A}(\mathbf{x})$ is the concentration gradient localization tensor. The volume averaging rule $\nabla \mathbf{C} = \langle \nabla c \rangle$ implies $\langle \mathbf{A} \rangle = \mathbf{I}$ (second order identity tensor), while the flux averaging rule $\mathbf{J} = \langle \mathbf{j} \rangle$ implies:

$$\mathbf{J} = -\mathbf{D}^{hom} \cdot \nabla \mathbf{C} \quad (79)$$

where the volume averaged flux $\langle \mathbf{j} \rangle$ and the concentration gradient $\langle \nabla c \rangle$ are equal to their macroscopic counterparts $\mathbf{J}$ and $\nabla \mathbf{C}$.

The homogenized diffusion tensor $\mathbf{D}^{hom}$ is then defined as:

$$\mathbf{D}^{hom} = \langle \mathbf{D} \cdot \mathbf{A} \rangle = \frac{1}{|\Omega|} \int_{\Omega} \mathbf{D}(\mathbf{x}) \cdot \mathbf{A}(\mathbf{x}) d\Omega \quad (80)$$

ensuring that the relationship between the macroscopic flux and concentration gradient is preserved (equation (79)).

VII.1.1.2- Eshelby Problem in The Case Of Diffusion

In an Eshelby problem, a single inclusion is embedded within an otherwise homogeneous, reference material. When a concentration gradient ∇C_{∞} is applied remotely to the infinite medium with diffusion coefficient D_0 , this inclusion with a different diffusion coefficient D_i alters the local concentration gradient, as illustrated in Figure 74.

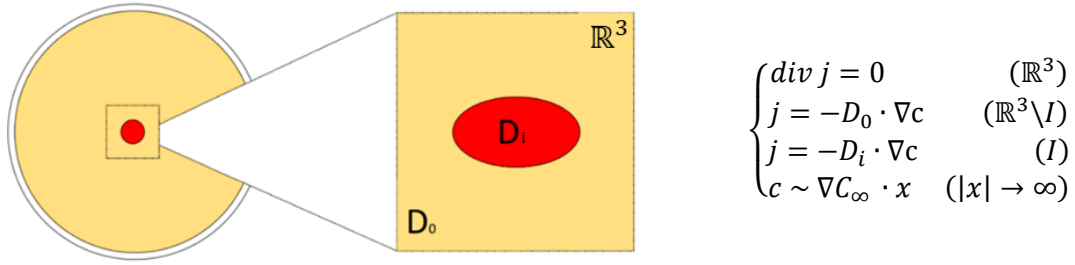


Figure 74: Eshelby's problem.

If the inclusion is ellipsoidal, the concentration gradient within the inclusion, denoted as ∇c_i , can be expressed using the following relation:

$$\nabla c_i = A_0^i \cdot \nabla C_\infty \quad (81)$$

Here, A_0^i is the concentration gradient localization tensor of the Eshelby problem, where 0 stands for the reference medium and i for the inclusion. It is expressed as:

$$A_0^i = [I + P_0^i : (D_i - D_0)]^{-1} \quad (82)$$

In this equation, I represents the identity tensor, P_0^i is the Hill tensor associated with the ellipsoidal shape of the inclusion and the diffusion coefficient D_0 of the reference medium.

The Hill tensor P_0^i plays a crucial role in the homogenization process, capturing the geometric shape of the ellipsoidal inclusion on the overall material response. This tensor is fundamental in linking the microstructural features to the macroscopic properties of the composite material [337].

The analytical expression for ∇c_i thus incorporates both the material properties and the geometric characteristics of the inclusion, as well as the properties of the reference medium.

The choice of the reference medium and that of the remote concentration gradient ∇C^∞ depends on the homogenization scheme. These choices represent indirectly the interactions between the inclusions used to represent the heterogeneities of the microstructure. Two homogenization schemes are now presented.

VII.1.2- Mori-Tanaka Scheme

The Mori-Tanaka scheme is suitable for a material consisting of a primary phase, known as the matrix, which contains various types of inclusions from other phases. This scenario is illustrated in Figure 75. The scheme is based on a specific application of Eshelby's problem, where the material phase m serves as the

matrix, and the remote concentration gradient ∇C_∞ is set equal to the average concentration gradient within the matrix. It is determined as a function of the macroscopic concentration gradient ∇C from the concentration gradient averaging rule.

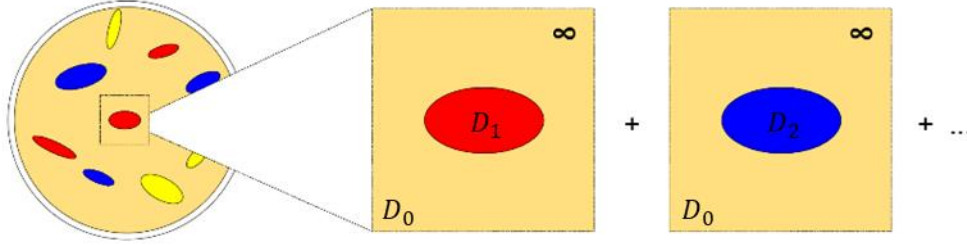


Figure 75: Representation of Mori-Tanaka scheme.

The fundamental principle of the Mori-Tanaka scheme involves the interaction between the matrix and the embedded inclusions. Each inclusion is considered to have an ellipsoidal shape, and the scheme aims to estimate the homogenized diffusion coefficient of the composite material by accounting for these interactions.

The Mori-Tanaka estimate of the homogenized coefficient D_{hom} is given by the following equation:

$$D_{hom} \approx D_{mt} = \langle D_i : A_0^i \rangle \cdot \langle A_0^i \rangle^{-1} \quad (83)$$

In this expression, A_0^i represents the concentration gradient localization tensor of the Eshelby problem for the inclusion i within the matrix 0 , and $\langle . \rangle$ denotes the volume averaging operation over all inclusions e.g. $\langle A_0^i \rangle = \sum_{i=0}^n f_i \cdot A_0^i$ where f_i is the volume fraction in the RVE of a phase represented by inclusion i . By abuse of notation, the matrix phase 0 is included in the sum, with the concentration: $A_0^0 = I$ where I is the identity tensor.

It is essential to rigorously evaluate the input data and the limits of the Mori-Tanaka scheme's applicability, referencing established literature. The following points are particularly pertinent:

- **Input Data Accuracy and Variability:**

The Mori-Tanaka method requires precise input data regarding the properties and distributions of inclusions. Variations in inclusion shapes, orientations, and volume fractions can significantly affect the accuracy of the homogenized properties. Further, non-symmetrical orientation distributions of ellipsoidal inclusions can lead to non-physical predictions, such as a non-symmetric diffusion tensor, which contradicts the physical expectation of symmetric diffusivity tensor in materials [338, 339].

- **Volume Fraction Limits:**

The applicability of the Mori-Tanaka scheme is generally valid for low to moderate volume fractions of inclusions. High volume fractions can lead to interactions between inclusions that are not adequately captured by the scheme, resulting in less accurate predictions. The aspect ratio of the inclusions also plays a crucial role; slender or highly elongated inclusions can lead to significant deviations from predicted behavior if their volume fraction increases beyond certain thresholds [340, 341].

- **Initial assumptions:**

Numerous studies have validated the Mori-Tanaka scheme for specific conditions and inclusion types. For example, studies [342–344] have shown that the scheme performs well under certain assumptions regarding inclusion shapes and orientations. However, deviations occur when these assumptions are not met.

VII.1.3- Self-Consistent Scheme

The self-consistent scheme is particularly effective for materials with polycrystalline or disordered microstructures, where no single phase dominates as matrix. This scenario is depicted in Figure 76. Unlike the Mori-Tanaka scheme, the self-consistent approach assumes that each inclusion is embedded in a reference medium that has the same properties as the homogenized material itself.

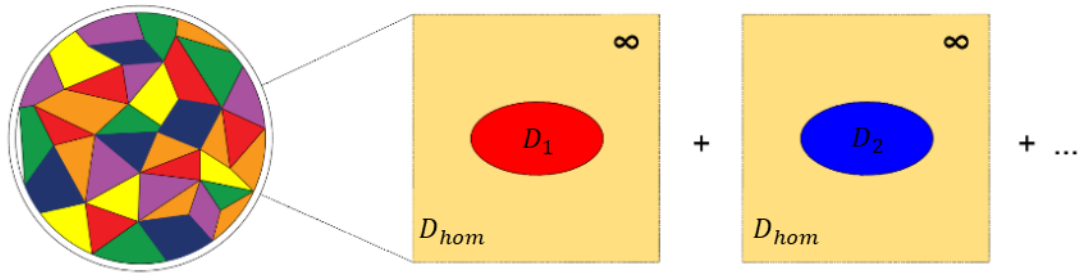


Figure 76: Representation of self-consistent scheme.

In this scheme, the overall homogenized properties are determined by the self-consistent closure equation (84). This equation can be solved by iteratively adjusting the matrix properties until self-consistency is achieved. The homogenized coefficient D_{hom} is determined as the solution to the following equation:

$$D_{hom} \text{ solution to } \langle (D_i - D_{hom}) \cdot A_{hom}^i \rangle = 0 \quad (84)$$

Here, A_{hom}^i represents the strain concentration tensor of the Eshelby problem for the inclusion i embedded in a reference medium whose diffusion coefficient is that of the homogenized material.

The self-consistent scheme accounts for the percolation effects of different phases within the material. Percolation refers to the formation of continuous paths through the material, which significantly influence the overall properties. This scheme considers the shapes orientation distribution and volume fractions of the inclusions to estimate their contribution to the homogenized diffusion coefficient of the material.

VII.2- Review Of Some Microstructure Models For Cementitious Materials

Numerical models, such as the CEMHYD3D hydration model by Bentz and Garboczi [112], enable detailed simulations on voxelized microstructures, offering insights into the diffusive properties of cement paste [345]. Ma et al. [190] utilized a two-scale numerical model to describe cement paste as a mix of capillary pores, unhydrated particles, and layers of high and low-density C-S-H. Walther et al. [346] employed Lattice Boltzmann simulations on 2D representative volumes, simplifying the microstructure into three phases: unhydrated particles, hydrates, and capillary pores, with phase volumes determined by Powers' hydration model [347]. Recent advancements in modeling have been reported in the literature. For example, approaches for modeling transfer phenomena have been introduced in [348–351]. Additionally, newly developed models for chemo-mechanical properties are discussed in [352, 353], while models addressing material failure can be found in [354].

We now review several multi-scale models for cementitious materials based on mean field homogenization, using the Eshelby based-schemes. Bernard et al. (2003) [10] introduced a multi-scale representation of OPC concrete to predict its mechanical properties. Their model is based on four distinct phases (Figure 77). Level I focuses on C-S-H gel properties derived from nano-indentation. Level II includes the C-S-H matrix, anhydrous grains, larger Portlandite crystals, and porosity, modeled using the self-consistent method due to the intertwined nature of hydrates. Level III represents mortar, comprising the cement matrix, sand particles, and transition zones, homogenized with a Mori-Tanaka model. Finally, Level IV represents concrete with granular inclusions within the cement matrix, also modeled using the Mori-Tanaka method.

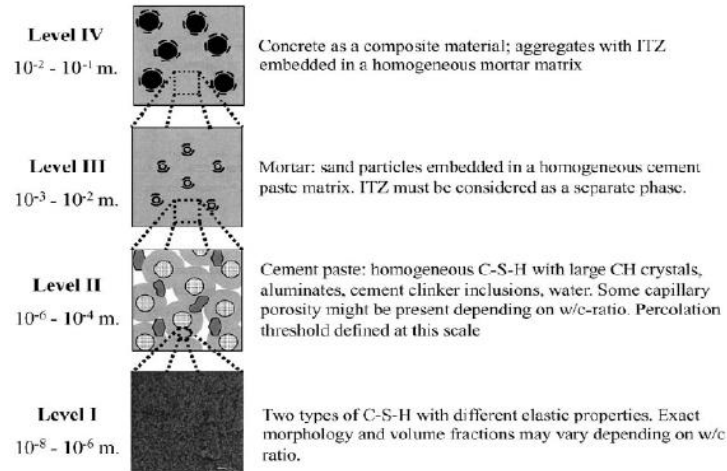


Figure 77: The multi-scale model proposed by Bernard et al. [10].

Pivonka et al. [355] pioneered the modeling of cement paste diffusion coefficient using mean field homogenization. Cement paste is modeled as a bi-phasic composite material using a differential scheme. In this model, capillary pores serve as the matrix while non-diffusive solid inclusions are dispersed within it. Based on this, Damrongwiriyanupap et al. [11] proposed an enhanced model where the cement paste is represented as a self-consistent assembly of spherical solid phases and cylindrical capillary pores (see Figure 78). However, this latter model predicts zero diffusivity for cement paste with a low water-to-cement (w/c) ratio, contrary to experimental findings which show a significant drop in the diffusion coefficient at such ratios, but non zero diffusion coefficients (see Table 24 - Table 27).

It should be noted that the model of Pivonka et al. [355] does not accurately represent the actual structure of cement paste. A direct application of these schemes to mechanical properties is inappropriate because a morphological representation consisting of a solid grain in a pore phase matrix does not hold significance for mechanical problems and results in zero mechanical strength. Therefore, it is essential to model transport properties using reliable models that reflect the physical and realistic characteristics of cement pastes.

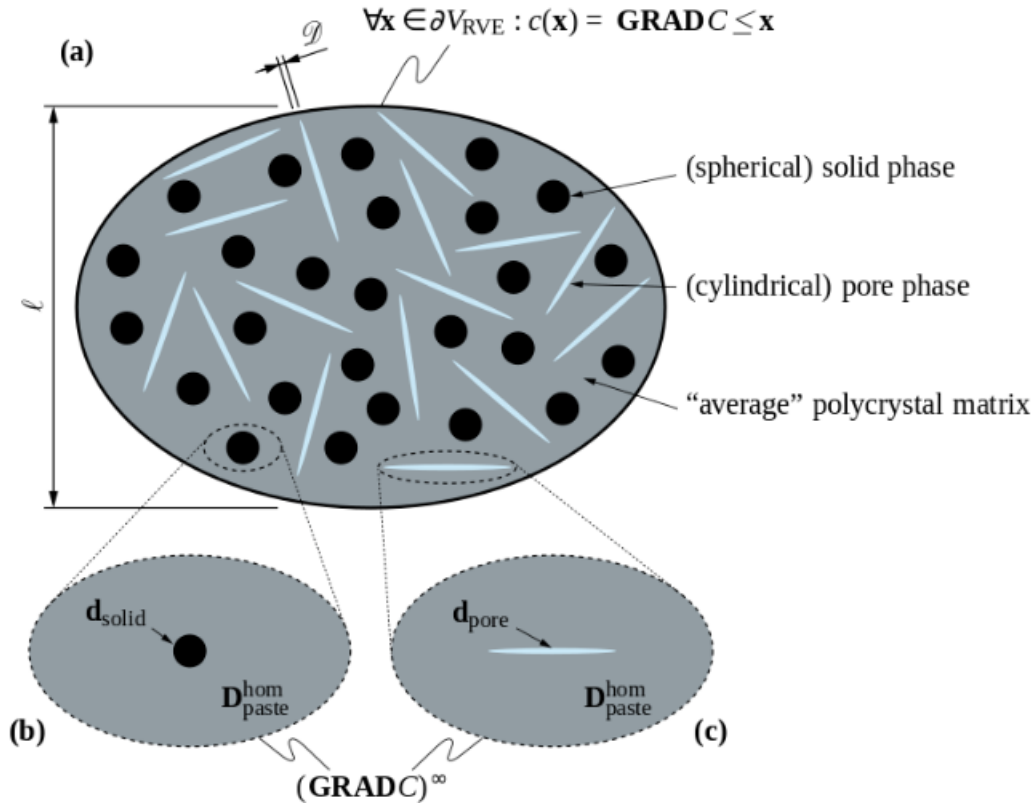


Figure 78: The diffusion model morphology proposed by [11].

Stora et al. [356] proposed an alternative approach for OPC pastes, suggesting that gel pores could serve as primary diffusion pathways in cement paste. They modeled capillary pores and certain hydrates (CH, AF) as inclusions in a low-density C-S-H gel matrix, via a Mori-Tanaka scheme at an intermediate scale. For the finer scale, they modeled the diffusivity of low and high-density C-S-H gels using a mixed assembly of composite spheres [357]. For the upper scale, clinker grains are considered as spherical inclusions surrounded by two layers, low density and high density layers as taken from Sanahuja *et al.* [210]. This approach, which integrates two types of composite inclusions—pores within a solid phase and solid particles within a porous phase—demonstrated good agreement with experimental data on water diffusion coefficients by assuming low diffusivity in C-S-H gel pores and bulk diffusivity in capillary pores instead of lower values as taken in the works of Pivonka et al. [355], Damrongwiriyanupap et al. [11].

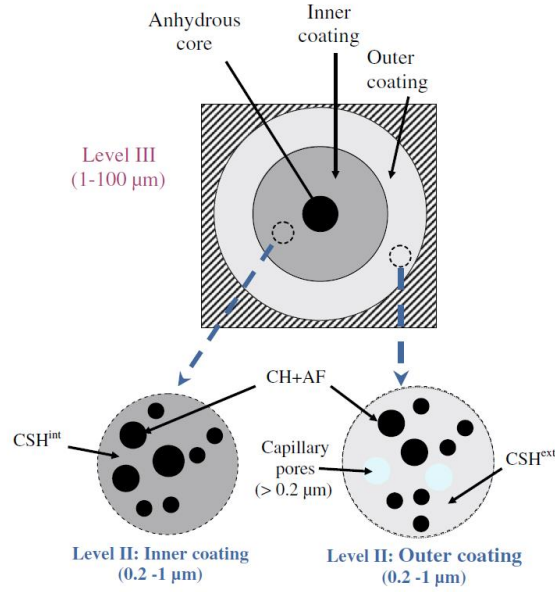


Figure 79: The multi-scale diffusion model proposed by Stora [356].

Honorio [358] utilizes Monte Carlo Micromechanics (MCM) and a self-consistent scheme to assess the electrical conductivity and resistivity of Portland concrete. The multiscale model (Figure 80) considers the variability in the microstructure of cement pastes, mortars, and concretes, particularly focusing on the pore solution conductivity evolution, which are crucial in determining the electrical response. The MCM approach allows for a probabilistic evaluation of how changes in clinker composition, hydration degree, and pore solution conductivity impact electrical properties across different scales. This method captures the complexity of the material's microstructure, from the nanometer-scale C-S-H phases up to the macroscopic concrete level. Additionally, the self-consistent scheme is applied to estimate the effective electrical conductivity of cement pastes, effectively capturing the transition from a liquid to a solid state as hydration progresses. This scheme assumes a random microstructure of spherical heterogeneities and demonstrates good agreement with experimental data, suggesting that more complex microstructural features such as inclusion shapes and orientations may not significantly affect the overall electrical properties.

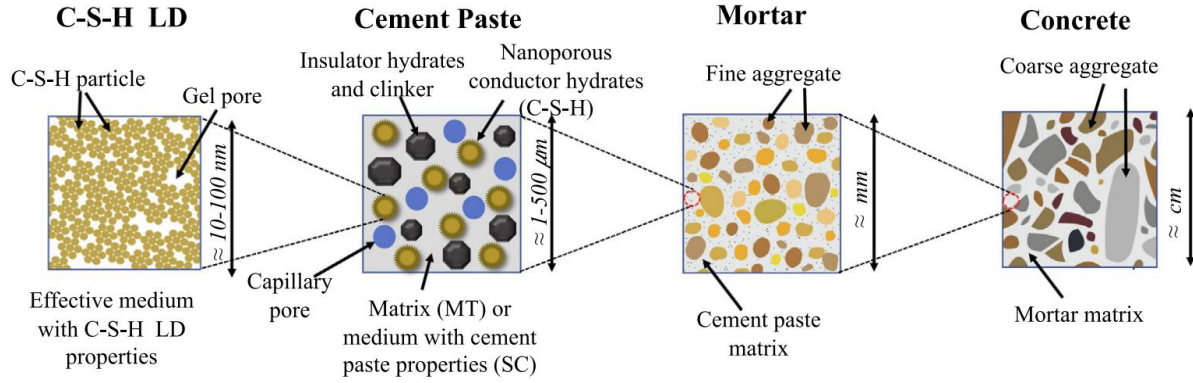


Figure 80: The multiscale microstructural model proposed by [358].

Honorio et al. [359] introduced various models to predict the elastic properties of Ordinary Portland Cement pastes using multi-scale homogenization techniques, as seen in Figure 81. These techniques allow for a detailed representation of the heterogeneous nature of cement paste, with different representations for the structure from the nanoscopic to the macroscopic levels. These models employ spherical inclusions to characterize the different phases such as C-S-H, unhydrated particles, capillary pores, and hydrates, while applying appropriate homogenization schemes. The models take as input parameters the volume fractions of the hydration products given by either Powers hydration model (Pow) [347], Königsberger-Hellmich-Pichler's model (KHP) [360], or Tennis and Jennings' hydration model (TJ) [83]. They are then categorized into one-scale (1s) and two-scale (2s) microstructural models. In the two-scale models, the C-S-H gel is represented at a lower scale than the cement paste itself, where a self-consistent homogenization is used. At the cement paste level, models use either the Mori-Tanaka (MT) or the Self-consistent (SC) scheme to predict the mechanical properties of the cement paste. The findings of this work underscore the importance of utilizing multi-scale models to achieve more precise predictions of the elastic properties of cement-based materials.

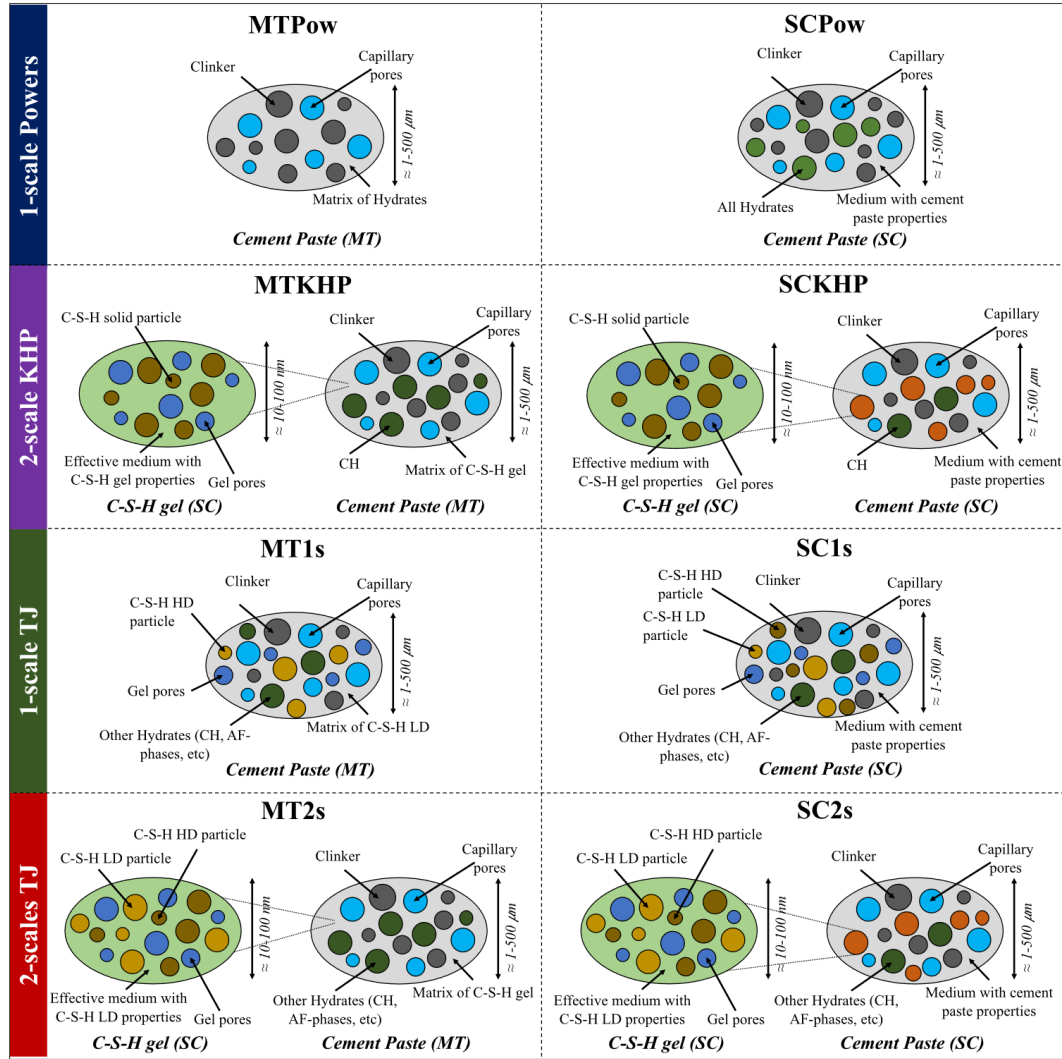


Figure 81: Multi-scale homogenization model for predicting the elastic properties of cement-based materials proposed by Honorio et al. [359].

Achour [9] developed a new paradigm for multiscale modeling, addressing both stiffness and diffusion coefficients of Portland cement paste using a unified microstructural description through Eshelby-based homogenization schemes. This model extends Pichler's approach by including detailed microstructural descriptions from Tennis and Jennings' findings [83]. The Pichler and Helmich model [361] includes two scale transitions focused on Ordinary Portland Cement paste with no addition. It relies on Powers' model for the computation of the volume fractions of hydrates, capillary pores and anhydrous clinker. Achour's models include a detailed version (3 scales) and a 2 scale version, the latter relying on a limited set of microstructural parameters for efficient computations. It describes the paste as a two-level structure, with capillary pores and hydrates at the smaller scale and clinker grains in a hydration foam matrix at the larger scale (Figure 82).

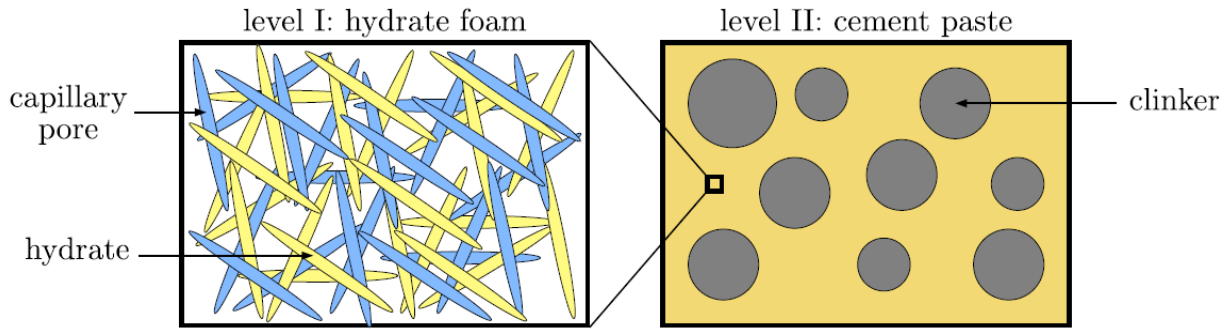


Figure 82: Representation of the two scales model proposed by Achour [9].

The detailed model represents three types of pores (gel, small, and large capillary pores) at three different scales to accurately describe pore network connectivity and solid phase percolation (Figure 83). The three levels are:

- Level 0: At the finest scale, high and low-density C-S-H gels are described as disordered assemblies of solid C-S-H bricks and gel pores.
- Level I: At an intermediate scale, the outer C-S-H layer is a mixture of small capillary pores (3-100 nm) and low-density C-S-H gel. The inner layer is considered a disordered mixture of high-density C-S-H gel and nano-sized crystalline hydrates.
- Level II: At the largest scale, large capillary pores (>100 nm) are considered as the remaining space between micro-sized crystalline hydrates, and composite inclusions representing clinker surrounded by an inner layer and outer C-S-H layer.

The self-consistent scheme is used at the three levels of the detailed model to account for the evolution of the connectivity of the pore and solid phases.

Both Achour's models account for both the decrease in diffusion coefficient and increase of stiffness throughout the hydration of cement paste. They have been validated on OPC pastes against experimental data for several w/c ratios, but cannot directly be used for slag-blended cement pastes. In the next section, these models will be modified to account for the effect of slag.

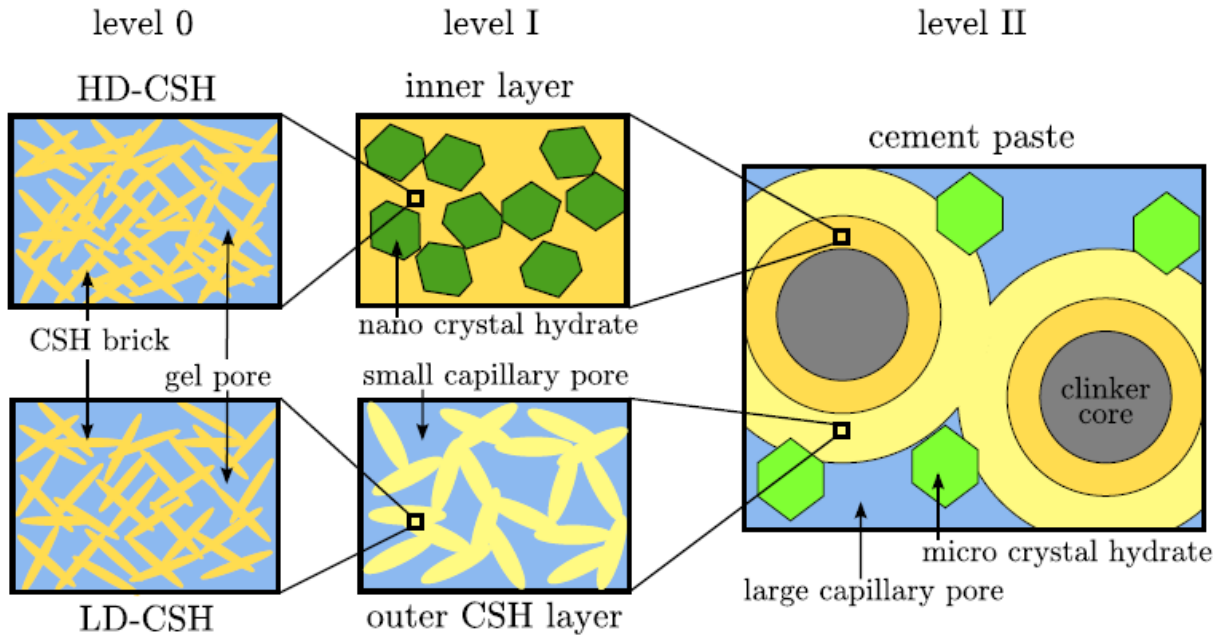


Figure 83: Representation of the detailed model proposed by Achour [9].

VII.3- Modelling strategy: development of a 2 scale homogenization model for slag blended cement pastes

VII.3.1- Methodology

Models based on the continuum micromechanics approach are efficient for integration into macroscopic models due to their analytical nature and reduced computational time. The strategy employed to develop these models encompasses several key steps:

- Firstly, it is necessary to propose a morphological model of slag blended cement paste that accurately describes the various solid and porous phases at appropriate scales. Such model considers the complex microstructure formed during hydration, including phases such as calcium silicates (C-S-H) and crystalline hydrates (CH, AFt, AFm ...) alongside the evolving pore network.
- The second step consists in selecting suitable homogenization schemes at each scale, with specific focus on ensuring connectivity of both solid and pore phases.
- The third step consists in determining the physical and geometric properties of each phase at the microscopic scale along with the phases volume fractions that can be calculated using

hydration models. This step is essential for establishing the input parameters required for the homogenization models.

- The last step consists in validating the model results through comparison with experimental data from literature studies on slag blended cement pastes. This validation covers diffusion properties over varying hydration times, water-to-cement ratios, and slag substitution levels.

VII.3.2- Development of an Analytical Multi-Scale Diffusion Model Incorporating Slag Substitution

To establish an analytical multi-scale diffusion model that takes the effects of slag substitution into account, an existing model developed by Achour [9] which has demonstrated reliability for CEM I pastes is considered. This choice was made not only because it is one of the most recent models in our literature review, but also because it integrates previous models and offers significant advantages in terms of both diffusion and elasticity modeling. This model serves as a reference regarding modifications and improvements proposed in the present study using the database presented in Table 26 and Table 27. We selected the two-scale model proposed by Achour as our baseline, rather than the three scale one, because it relies on a more limited set of model parameters.

In the development of our model for diffusion coefficients, we extensively explored several alternative approaches in a trial and error process, involving the testing of various hypotheses to find the most reliable configuration. The process involved testing different model variants, each with its own set of advantages and limitations, which were instrumental in guiding us toward the final, optimized model. By evaluating approaches such as using the Mori-Tanaka or the Self-Consistent scheme, Ma et al.'s introduced porosity differentiation, and investigating the best scale at which crystalline hydrates should be modeled, we were able to identify key factors influencing diffusion coefficients and address specific challenges.

The models discussed in the following analysis will be referred to with the numbering system as follows:

- Model (1) the baseline Mori-Tanaka model (see Figure 84),
- Model (2) the Self-Consistent model,
- Model (3) the Self-Consistent model including a porosity distinction,
- Model (4) the Mori-Tanaka model with non-porous hydrates as larger-scale particles.

These models will be compared to experimental measures of D_{eff} for OPC pastes at the beginning, and the most promising model (highest R^2) will be adapted to include slag substitution. The model with the highest R^2 value will serve as a reference against which the performance of the remaining models will be evaluated. For example, if Model (1) exhibits a higher R^2 than Model (2), it will be used as the benchmark when evaluating Model (3), and this process will continue for all four models.

In this section, we used experimental data from the database presented in Table 26 and Table 27, both of which provide effective diffusion coefficients. Volume fractions of each of the phases are computed using the hydration model of Chapter IV. In the comparison with experimental D_{eff} , for each data point, the chemical composition of slag and clinker, their fineness, the slag substitution rate, the w/b ratio and the curing time and temperature provided in the corresponding references have been used to model hydration and calculate the volume fractions at the time of testing. When explicit chemical compositions were not available, average compositions for clinker and slag were used in the hydration modeling and data analysis (for clinker: $m_c = 64\%$, $m_s = 21\%$, $m_A = 5\%$, $m_M = 2\%$, $m_{\bar{s}} = 3.3\%$, $m_F = 3\%$; and for the slag composition: $m_c = 41.2\%$, $m_s = 35.8\%$, $m_A = 14\%$, $m_M = 8.2\%$, $m_{\bar{s}} = 0.1\%$, $m_F = 0.25\%$). The selected data were those cured at ambient temperature (between 20 and 25° C) and those corresponding to hydration periods longer than 10 days. The databases used for this section is categorized into two groups: pastes without slag substitution (database P_0 , 55 data points) and pastes with slag substitution (database P_λ , 15 data points). The combined dataset is referred to as database P_{all} (70 data points in total). Only datapoints from P_0 are used in this section.

VII.3.2.1- Model (1): Model using Mori-Tanaka scheme

As detailed in section V.2.3-, slag substitution significantly affects the microstructure and density of calcium silicate hydrate (C-S-A-H gels), which in turns modifies the diffusion coefficient of C-S-A-H gels. Other hydrates are well crystallized and assumed non porous, therefore do not contribute to diffusion. Moreover, it was mentioned in section V.2- that slag substitution primarily modifies the porosity network within the C-S-A-H gel (pores smaller than 3 nm) while reducing the number of large capillary pores (pores larger than 100 nm).

To enhance the 2 scale model proposed by Achour, a critical distinction between the different hydrate phases is thus made here. Achour's model considered all hydrates as a single phase, representing them collectively with capillary pores as part of the hydrate foam. Since this approach considers all hydrates as having identical diffusion coefficients and geometrical properties, it does not reflect the difference between crystalline and porous hydrates. Models (1) divides hydrates into crystalline and porous (C-S-H and C-S-A-H gels) categories (Figure 84).

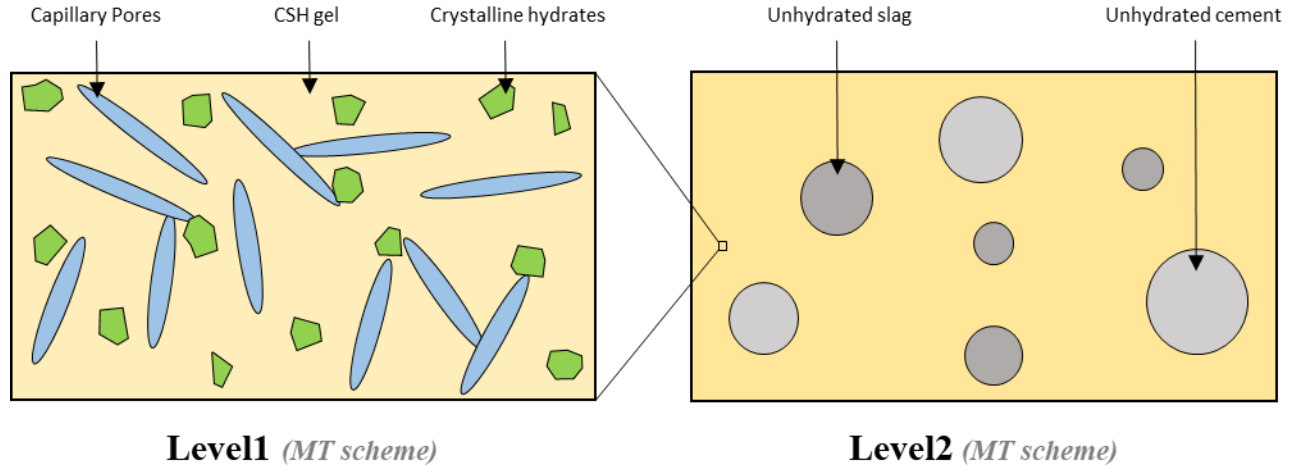


Figure 84: Representation of the diffusion 2 scale proposed model (1).

Model (1) is structured as follows:

- **Level 1:** The hydrate foam is depicted as a matrix inclusion composite, where the C-S-H gel is the matrix embedding inclusions of capillary pores and crystalline hydrates. The diffusion coefficient of capillary pores is set equal to the bulk diffusion coefficient of Cl^- in free solution ($2.1 \times 10^{-09} \text{ m}^2/\text{s}$ at 25°C). The geometrical aspect ratio of the spheroid used to represent capillary pores is set to 7, reflecting an elongated structure consistent with its actual morphology as considered by Achour [9]. Crystalline hydrates, encompassing Afm, Aft, monoc, AH, HT, Portlandite, and HG, are modeled as spheres to reduce the number of model parameters ($\omega = 1$). A sensibility analysis was done to test this hypothesis during the model development: case 1 where all the crystalline hydrates were spheres ($\omega = 1$), case 2 where the crystalline hydrates were prolate shape $\omega = 10$, case 3 where the crystalline hydrates were considered of an oblate shape $\omega = 0.1$. An isotropic distribution of orientation of crystalline hydrates and pores is assumed in all cases. The hypothesis to take the crystalline hydrates as spheres ($\omega = 1$) was confirmed to be reliable in the modeling process. The diffusion coefficient of this phase was assumed to be 0 given that the diffusion cannot take place in non-porous crystalline phases. The diffusion coefficient of C-S-H gel was determined through subsequent analysis.
- **Level 2:** At this level, the hydrate foam acts as the matrix, with unhydrated grains treated as inclusions. These grains are modeled as spheres ($\omega = 1$) since experimental observations discussed in the clinker microstructure section V.1.1- show they are neither flat nor elongated. They are considered non-diffusive phases.

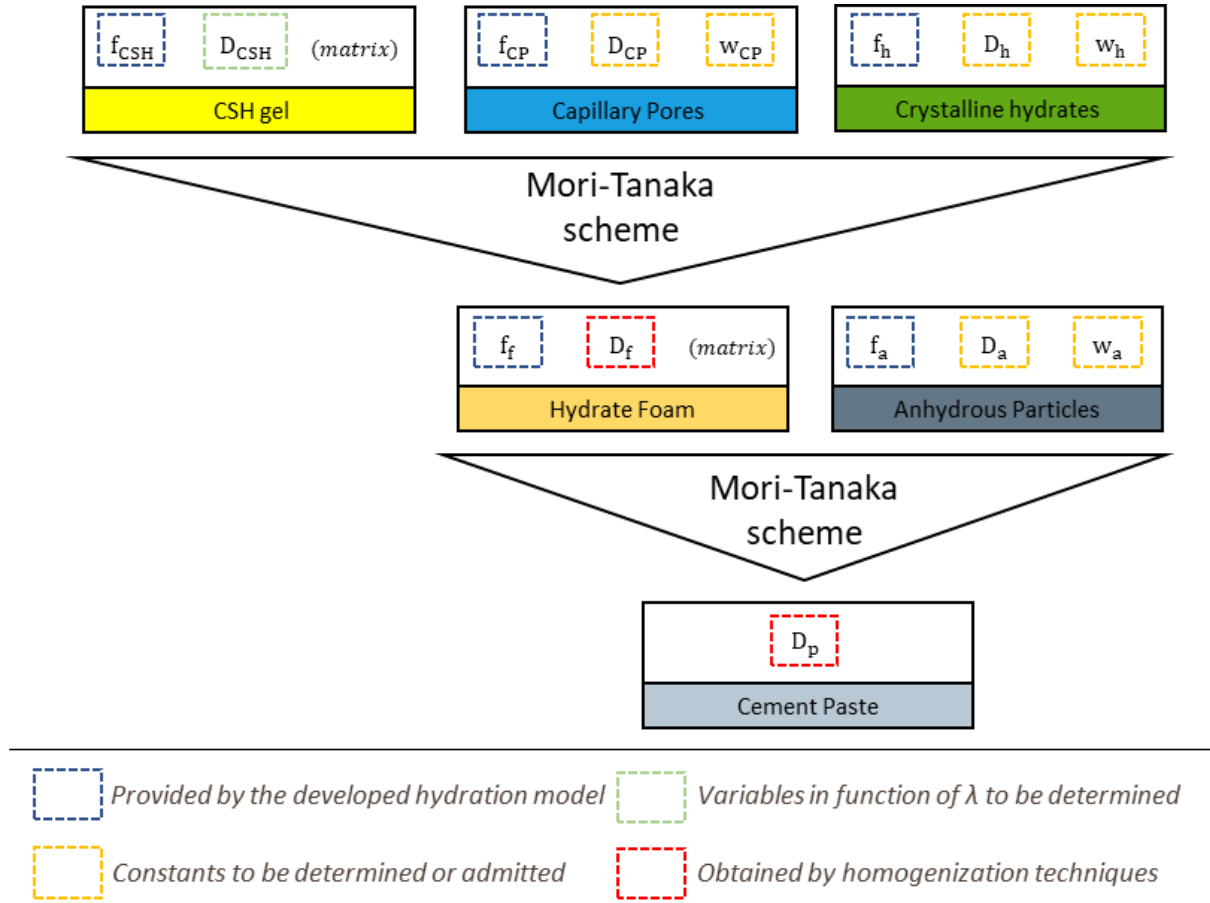


Figure 85: Flowchart of computation for model (1) for diffusion.

The time dependent volume fractions $f_i(t)$ for the model were derived from the developed hydration model from Chapter IV (e.g. Figure 37). Detailed parameters are presented in Table 28.

The two scales model developed				
	C-S-H gel	Capillary pores	Crystalline hydrates	Anhydrous particles
$f_i(t)$ [-]	The developed hydration model in Chapter IV			
D_i [m ² /s]	2.53E-12*	2.10E-09	0	0
ω_i [-]	(matrix)	7	1	1

**this value is for model (1) only, and will be adjusted for other subsequent multi-scale models*

Table 28: Parameters of the model (1).

The development of the model starts with the verification of its capability to predict the effective diffusion coefficient in cement paste without slag substitution.

Since slag substitution influences the structure and density of C-S-A-H gel, we must define C-S-A-H gel characteristics as function of the slag substitution rate λ . It is expected that C-S-A-H gel with a similar structure and composition will have consistent diffusion coefficients. Hence, C-S-H gel formed from the hydration of pure clinker is assumed to exhibit the same diffusion coefficient regardless of other parameters. By inversion of the multi-scale model (1) for the previously selected 55 measures of the database P0 with T_{cure} in [20°C-25°C] and $t_{cure} > 10$ days, we narrowed down the diffusion coefficient range for C-S-H gel in CEM I between 0.5E-12 and 4.5E-12 m²/s, with a retained mean value of 2.53E-12 m²/s. This value is consistent with literature values for C-S-H diffusion coefficients (between 8.3E-13 and 1.04E-10, from [359, 362–365]).

When applied to database P_0 , model (1) with the calculated C-S-H diffusion coefficient yielded an R^2 value of 0.77. Figure 86 shows the predicted versus experimental diffusion coefficients for pastes in P_0 . The closer the data points are to the diagonal line ($y=x$, indicating $D_{model} = D_{experimental}$), the more reliable the model is. When data points are above this line, the model overestimates the results, and conversely. Notably, the data points cluster tightly around the diagonal line, indicating the model's reliability.

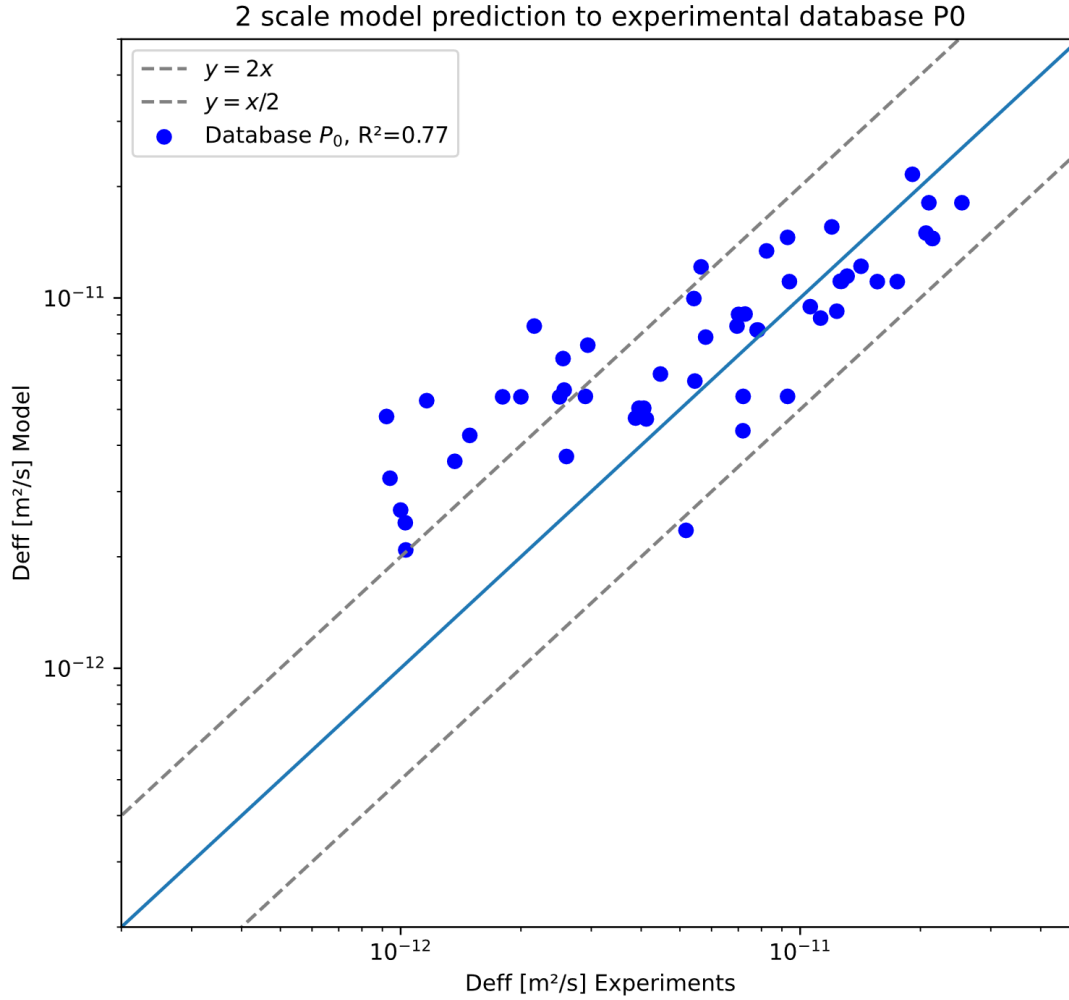


Figure 86: Comparison the model (1) to experimental data, for database P_0 (55 data points).

For the time being, model (1) will be used as a reference when assessing the pertinence of model (2).

VII.3.2.2- Model (2): Model using Self-Consistent Scheme

One important alternative explored was the use of a self-consistent scheme to upscale the properties of crystalline hydrates, C-S-A-H, and capillary pores to the hydrate foam level, instead of involving the Mori-Tanaka scheme. The self-consistent scheme offers several advantages in this context. Unlike the Mori-Tanaka approach, which treats the C-S-A-H gel phase as a matrix, model (2) considers each phase of the composite material as if it were embedded within the effective medium, following the self-consistent scheme. C-S-H gel particles are modeled as spheroids, all with the same aspect ratio w_{CSH} , with an isotropic distribution of orientation. This approach is schematically depicted in Figure 87 and Figure 88.

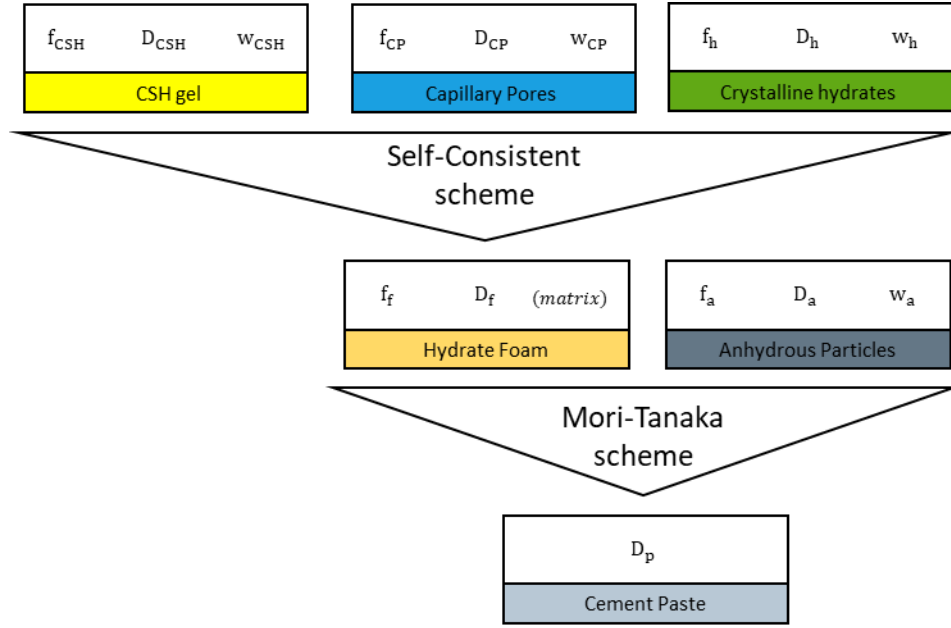


Figure 87: Flowchart of computation for model (2) for diffusion.

This model however introduces an additional parameter: the geometrical aspect ratio of C-S-A-H. The application of this model to CEM I-based materials (without slag addition) yielded results presented in Figure 89, with these parameters: $\omega_{CSH\ gel}=1E-3$ (the best fit among values within the interval $[1E-3,1E1]$. Selecting smaller values does not significantly affect the results, as the asymptotic regime for $\omega \rightarrow 0$ is nearly reached at this point), $\omega_{CP} = 7$ (fixed), $D_{CSH} = 4.8E - 13\ m^2/s$ (fitted), $D_{CP} = D_{bulk}$ (fixed), and spherical non diffusive crystalline hydrates. Note that the change of homogenization scheme lead to the adjustment of CSH gel at a value almost 5 times lower for the Self-Consistent scheme than for the Mori-Tanaka one.

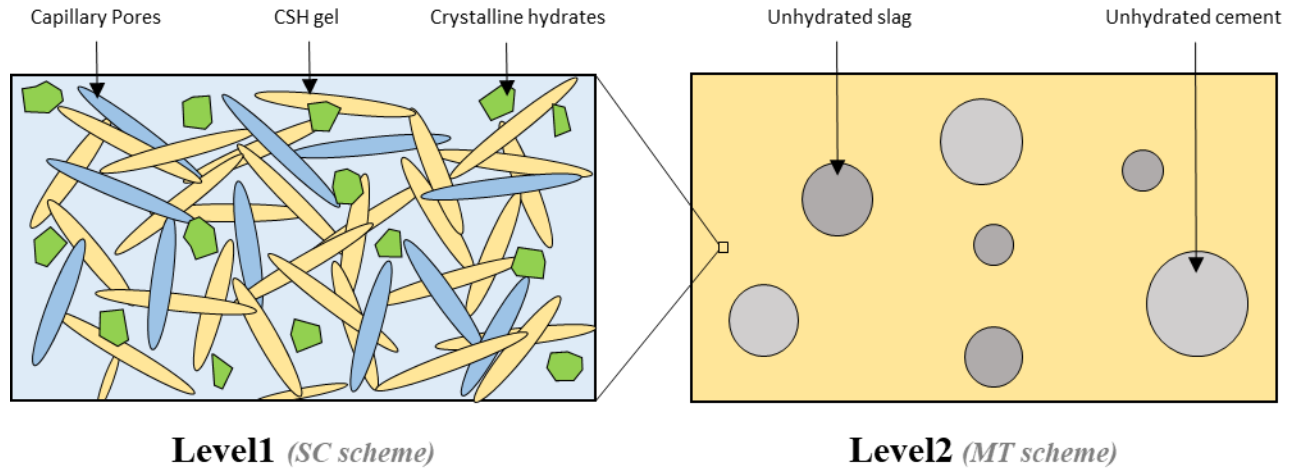


Figure 88: Representation of the diffusion 2 scale proposed model (2).

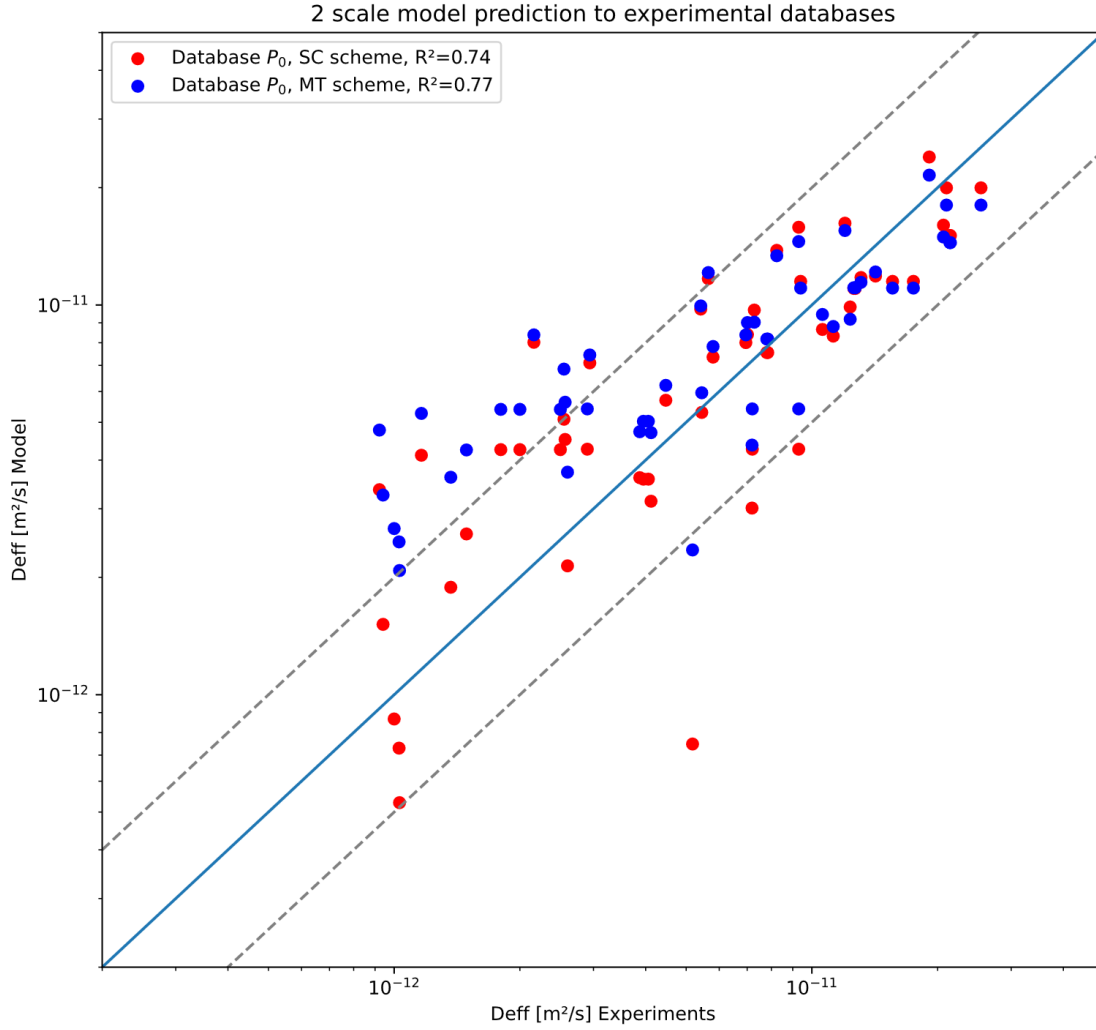


Figure 89: Comparison of model variants (1) and (2) to experimental data, for cement with no slag substitution (55 data points).

In general, C-S-H gel is typically modeled as a thin, layered structure with interstitial porosities. A parametric study indicated that the parameter $\omega_{CSH\ gel}$ required to have the best adjustment with experimental data is notably low, suggesting that it should be treated as the matrix. The value $\omega_{CSH\ gel} = 1E - 3$ implies an unrealistically flattened C-S-H gel particle shape, which is not representative of its actual morphology. The self-consistent may not be the most appropriate method for upscaling in this context. The Mori-Tanaka scheme, on the other hand, has proven to be more effective in this context. Despite this limitation, the model produced an R^2 value of 0.74 on P_0 , which is comparable to the value achieved by model (1).

However, the performance of model (2) when slag was incorporated was not taken into account. Given its slightly lower reliability compared to model (1), it was ultimately excluded from further analysis involving slag-blended cements. Model (1) is still used as a reference when assessing the pertinence of model (3).

VII.3.2.3- Model (3): model using Self-Consistent scheme, with a capillary porosity partition

Another model considered is based on the partition of the capillary porosity brick into small capillary pores (considered in level 1 of model (1)) and large capillary pores (considered in level 2 of model (1)). This distinction is made based on the work of Ma et al. [190] (Appendix B). This model's schematic representation is provided in Figure 90. By partitioning the porosity into these two categories, model (3) aims to better account for variations in pore structure and their impact on diffusion coefficients. The transition between the lowest level to the hydrate foam level was made using the Self-Consistent scheme. The diffusion coefficient of both small and large capillary pores is fixed at the value of D_{bulk} . This is because the ion retardation effects in pores occur over distances of only 5 to 10 angstroms, which is negligible within capillary pores of larger dimensions. Therefore, these effects do not significantly impact ion diffusion within the capillary pore network. The calibration of this model on the database P_0 resulted in the following parameters values: $\omega_{csh} = 1E - 3$, $\omega_{SCP} = 13.46$, $\omega_{LCP} = 1$, $D_{CSH} = 2.35E - 13$, while other parameters remained unchanged ($\omega_h = 1$ and $D_h = 0$) and $D_{SCP} = D_{LCP} = D_{bulk}$ fixed as discussed before.

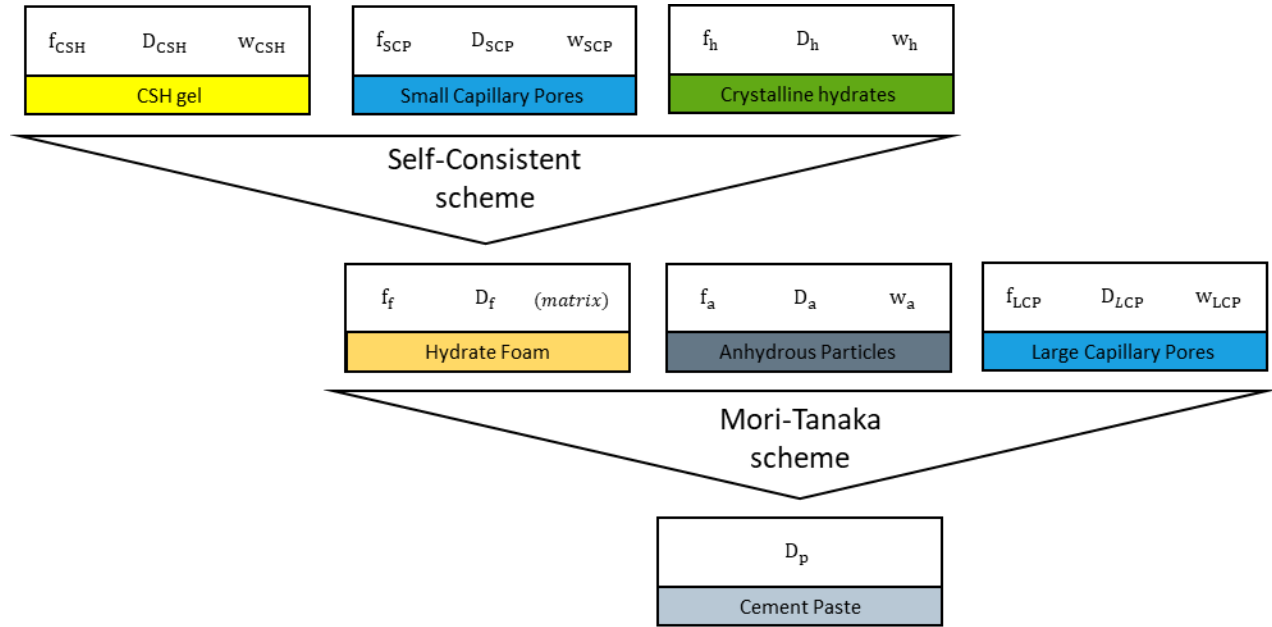


Figure 90: Flowchart for the multi-scale model (3) with two capillary pore size.

The results of this approach are illustrated in Figure 91, where the modeled diffusion coefficients are compared with experimental measurements and with model (1). This model achieved an R^2 value of 0.74, which is also slightly lower than that of model (1).

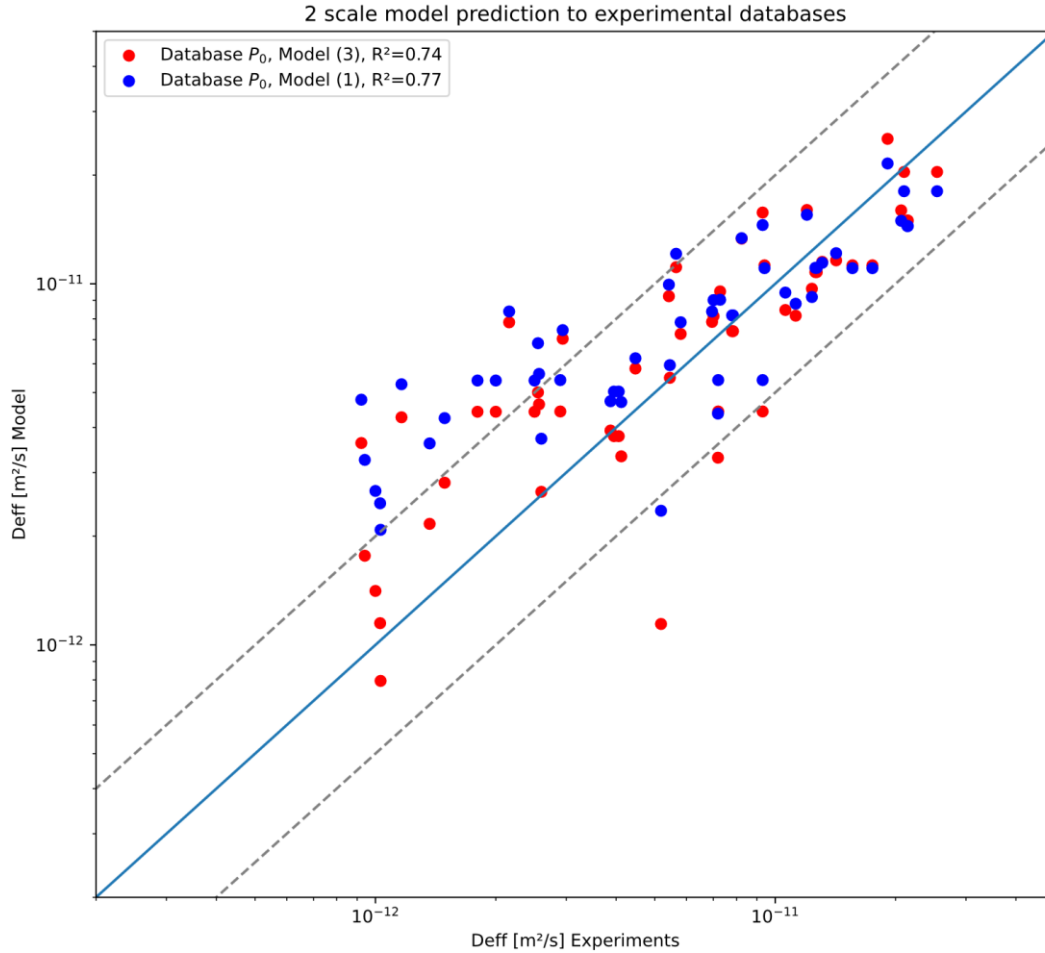


Figure 91: Comparison of model (3) to experimental data and to model(1) results; on database P_0 .

The decrease in R^2 indicates that while model (3) captures some of the diffusion characteristics, it does not fully align with the observed data across all scenarios. Further analysis is done section VII.3.3-. Consequently, despite its potential, this model was deemed less effective than the model (1) and was subsequently disregarded. Model (1) is therefore still used as a reference when validating the next model.

VII.3.2.4- Model (4): model using Mori-Tanaka scheme, with crystalline hydrates at the cement paste level

Another hypothesis involved modeling non-porous hydrates as larger-scale particles placed at the upper scale instead of the lower scale, as depicted in Figure 92. This approach assumes that in some cases, the size of hydrate particles can potentially be comparable in size to the anhydrous particles. Indeed, SEM

observations also show CH crystals at the scale of the anhydrous cement particles. Thus, it is legitimate to investigate if considering hydrates as part of the upper scale might improve the accuracy of diffusion coefficient predictions.

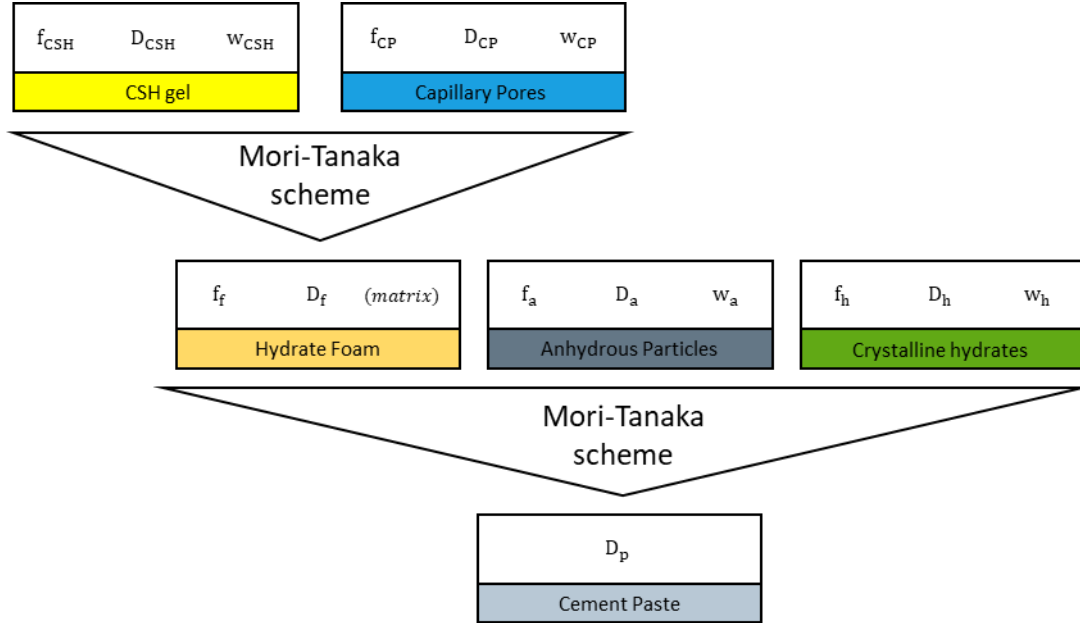


Figure 92: Flowchart for the model (4) if non-porous hydrates were taken as larger-scale particles instead of the lower scale.

The calibration of model (4) on the database P_0 resulted in the following parameter values: $D_{CSH} = 1.68E - 12$ m²/s, while other parameters remained unchanged ($\omega_{CP} = 7$, $\omega_h = 1$, $D_{CP} = D_{bulk}$ and $D_h = 0$).

This modification significantly lowered the adjusted diffusion coefficient of C-S-H gel (up to tenfold), resulting in a less realistic model with an R^2 of 0.73 (Figure 93). Given the reduced accuracy for P_0 diffusion coefficient compared to model (1), this hypothesis was excluded from further consideration.

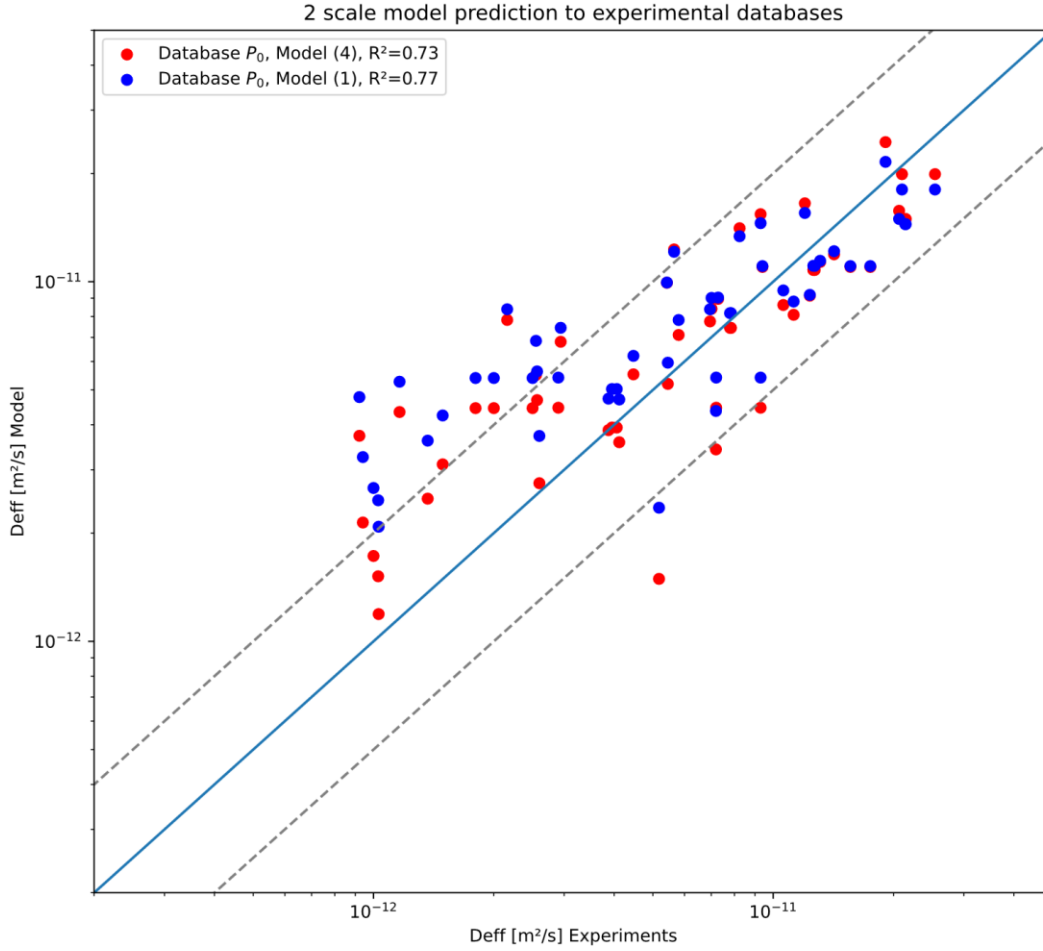


Figure 93: Comparison of the model (4) to experimental data and to model (1) on database P_0 (55 data points).

VII.3.3- Comparative Analysis

To evaluate the reliability of the model proposed in this study, we compared the R^2 value with the two scale model developed by Achour (morphological model with undifferentiated hydrates, Self-Consistent at level I and Mori-Tanaka at level II, the volume fractions calculated using Powers model, diffusion coefficients and aspect ratios as given in [9]) using database P_0 , as shown in Figure 94. Although Achour's model is reliable for the restricted dataset provided in this reference, its reliability diminishes when applied to the larger P_0 database, which includes part of Achour's original dataset. Our model demonstrates greater reliability across this expanded dataset.

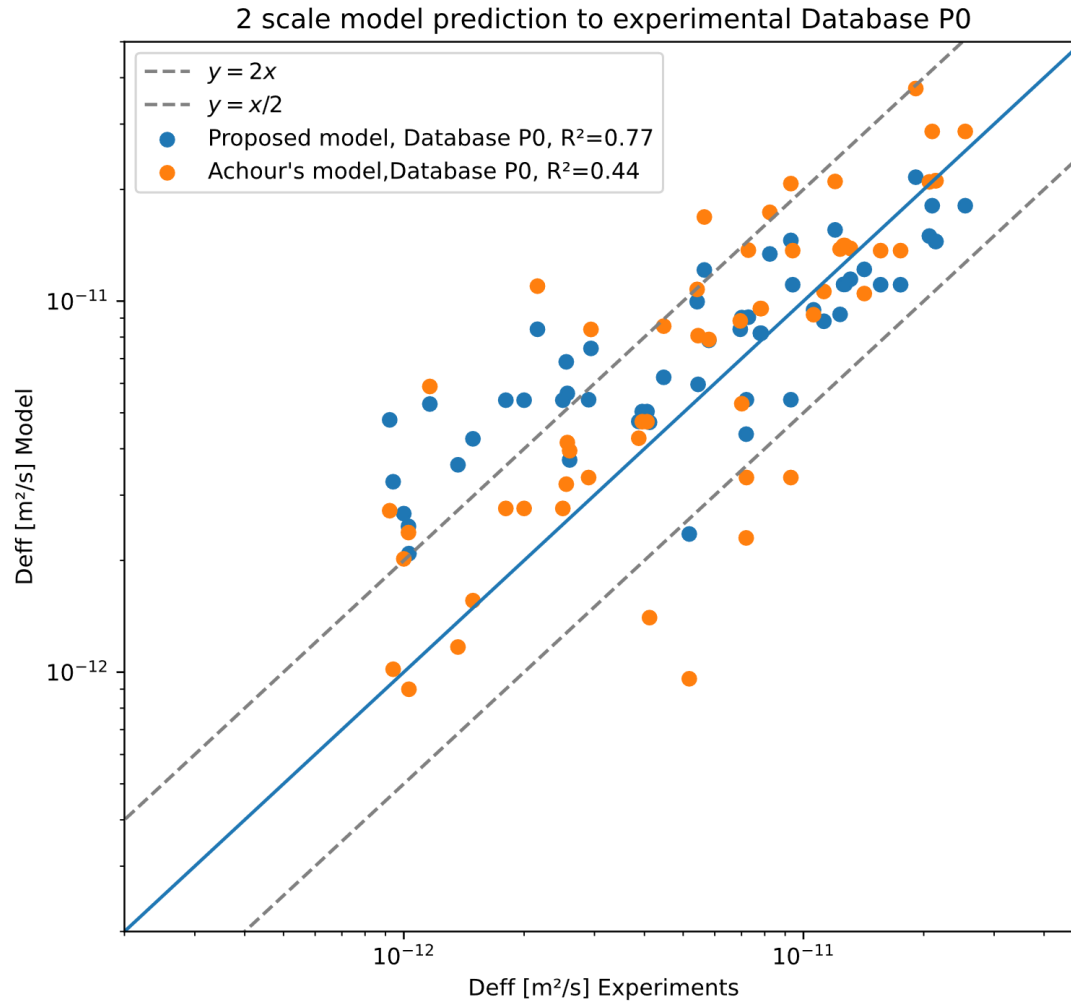


Figure 94: Comparison between Achour's model and the 2 scale proposed model to experimental data, for cement with no slag substitution.

A comparative analysis of the proposed models is next carried out using key statistical factors including R^2 , RMSE, MAE, MAPE, SMAPE, as well as their normalized versions (Table 29) (see Appendix D for more details). These metrics offer insight into the models' accuracy and reliability when predicting diffusion coefficients in various cementitious systems.

		R ²	RMSE	MAE	MAPE	SMAPE	RMSE normalized	MAE normalized
		[-]	E-12 [m ² /s]	E-12 [m ² /s]	[%]	[%]	[-]	[-]
Model (1)	P_0	0.77	3.49	2.96	78.43	48.16	0.44	0.37
Model (2)	P_0	0.74	3.25	2.60	52.88	41.03	0.41	0.33
Model (3)	P_0	0.74	3.24	2.59	53.92	39.79	0.41	0.33
Model (4)	P_0	0.73	3.34	2.67	57.56	41.18	0.42	0.34

Table 29: Comparative Performance of Various Models on OPC and Slag-Blended Cementitious Systems.

First, the initial decision to continue working with Model (1) was based solely on its relatively high R^2 values, with a coefficient of determination of 0.77 for the P_0 dataset, suggesting a strong ability to explain data variability in OPC pastes. However, when evaluating other error metrics such as RMSE, MAE, MAPE, and SMAPE, Model (1) underperforms compared to the other models. For instance, Model (2) and (3) demonstrates superior performance across these indicators, with fewer biases and errors in predictions.

This highlights the limitation of relying solely on R^2 for model evaluation. Despite this, Model (1) was chosen for further work involving slag incorporation due to time constraints and the decision was made early in the study.

In retrospect, it may not have been the most judicious choice to prioritize R^2 without considering other error metrics. Nonetheless, the methodology developed for Model (1) can be applied to other models in the future. Although it was not possible to extend Model (2) and (3) to slag-blended pastes within the current timeframe, it remains a promising alternative for future studies.

In conclusion, while Model (1) was originally selected for its R^2 , further analysis shows that Model (2) and (3) outperforms it across other statistical parameters. This acknowledgment does not diminish the value of the current work but highlights areas for potential improvement. Future efforts will focus on extending the methodologies developed for Model (1) to the other better-performing models.

VII.3.4- Impact of Slag Substitution on Diffusion Coefficients: Model Extension

The next phase involves expanding model (1) to incorporate the effect of slag substitution. The introduction of slag into the cement paste not only modifies the quantity of formed phases, as discussed in the Chapter IV, but also modifies the chemical composition and characteristics of the C-S-A-H gel phase, as detailed in the section V -. These changes necessitate adjustments to the model parameters while maintaining certain assumptions:

Level 1:

- The diffusion coefficient of capillary pores remains equal to the bulk diffusion coefficient of water, which is $2.1\text{E-}09 \text{ m}^2/\text{s}$, with a geometrical aspect ratio equal to 7.
- The hydrated crystals are modeled as spherical inclusions with a diffusion coefficient of zero.
- While the diffusion coefficient for C-S-H is established at $2.53\text{E-}12$, the corresponding coefficient for C-S-A-H, which forms in the presence of slag, remains undetermined and requires further investigation.

Level 2:

- Unhydrated clinker grains are treated as spherical inclusions without any diffusion coefficient inside the hydrate foam matrix

To assess the impact of slag substitution, we performed a reverse analysis to estimate the C-S-A-H gel diffusion coefficient using the multi-scale model to each data point in the slag-substituted dataset (P_λ). The results, plotted against the slag substitution rate (λ) in Figure 95, show a significant decrease in the diffusion coefficient of C-S-A-H gel with increasing slag content. This trend was fitted using an exponential equation for the black 3 points data (taken for the same composition at $\lambda=0.5, 0.65$ and 0.7), then validated using the blue points data. The value of D_{CSH} for $\lambda=0$ is taken $2.53\text{E-}12$ as found previously in model (1) for CEM I. This fitting provided a functional relationship between the C-S-A-H gel diffusion coefficient and the slag substitution rate.

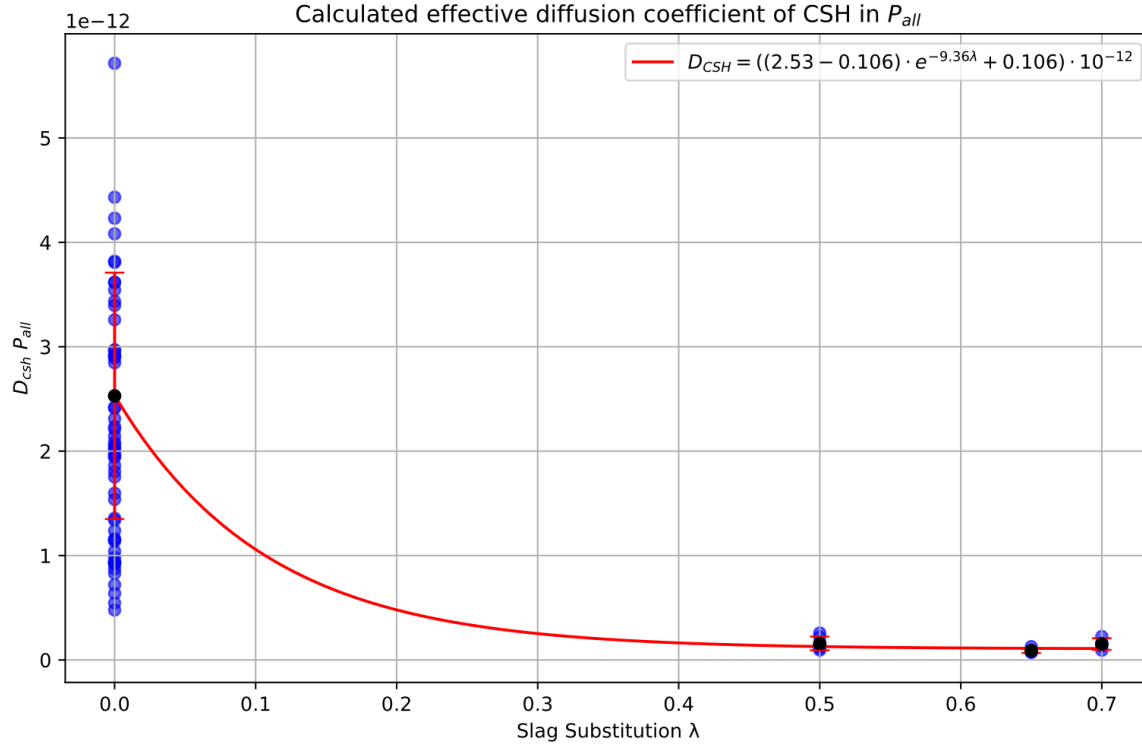


Figure 95: Mean and standard deviation of the calculated diffusion coefficient of C-S-A-H gel obtained by reverse analysis of the model (1), with a fitted model to assess the diffusion coefficient of C-S-A-H gel in function of slag substitution λ .

Note that the variability of $D_{CASH\ gel}$ is low for λ in $[0.5, 0.7]$, which suggest that $D_{CASH\ gel}$ could be modeled as intrinsic material parameter related to λ only.

The exponential fit yielded the following equation for the C-S-A-H gel diffusion coefficient, (D_{C-S-H}):

$$D_{CSH} = [(2.53 - 0.106) \cdot \exp(-9.36 \cdot \lambda) + 0.106] \times 10^{-12} \text{ m}^2/\text{s} \quad (85)$$

Note that, due to the absence of data point for λ between 0 and 0.5, the value -9.36 controlling the decay in the exponential term may not be applicable in that range. Further analysis with additional datapoints would be required, unfortunately no references have been found for D_{eff} on slag blended pastes with $\lambda < 0.5$.

Another note is that, when applying in model (1) a constant $D_{CSH\ gel}$ value of $2.53 \times 10^{-12} \text{ m}^2/\text{s}$ (as determined from the clinker-only dataset P_0) on the slag-substituted dataset (P_λ), an unsatisfying fit with a negative R^2 value resulted (-1.47E3). However, the application of exponential equation for $D_{CSAH\ gel}$ results in a raised value of $R^2 = 0.53$, indicating a better alignment between the model predictions and the experimental data.

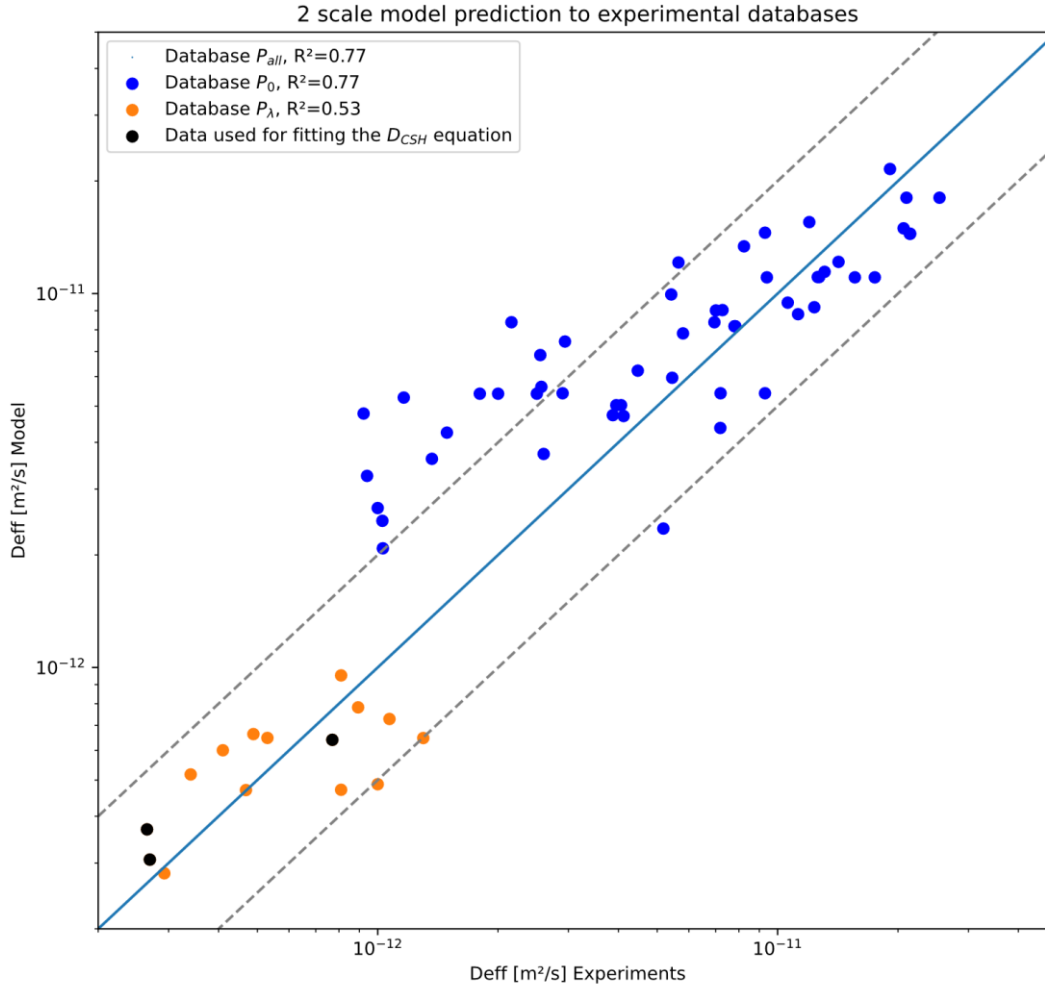


Figure 96: Comparison of model (1) with a variable D_{CSH} to experimental data, for OPC (points in blue) and with slag substitution (points in orange) along with the data used for fitting equation (85) (points in black).

Figure 96 illustrates the reliability of model (1) with a variable D_{csh} (equation (85)) by showing the predicted diffusion coefficients for both slag-substituted and non-slag-substituted data points. The R^2 values for the datasets P_0 (clinker-only, 55 datapoints), P_λ (slag-substituted, 15 data points), and P_{all} (combined, 70 data points) are indicated, demonstrating the model's overall performance for different conditions. Data points used to fit equation (85) are also indicated.

The extended model (1) reflects a more accurate representation of the diffusion processes in cement pastes with varying slag content, highlighting the significant role of slag in modifying the microstructure and transport properties of C-S-H. This refined model provides a tool for predicting the behavior of slag-blended cement pastes.

To further validate the developed two-scales diffusion model (1), the evolution of the effective diffusion coefficient over time was compared with experimental results. Figure 97 illustrates the experimental data measured by Ngala [292] for a slag substitution of 0 and 0.65 and varying water-to-binder ratios (w/b) of 0.4, 0.5, 0.6, and 0.7, observed at 85 days. Additionally, Figure 98 displays data provided by Wilson [301] for a slag substitution of 0.5 with w/b ratios of 0.4 measured at 28 and 210 days. It shows also the modeling evolution of the diffusion coefficient over time. Both datasets demonstrate that the model reproduces relatively well the experimental observations and accurately reflects the fact that an increase in the water-to-binder ratio leads to an increase in the diffusion coefficient. Furthermore, Wilson's data across different times (28 and 210 days) confirms the model's capability to predict a decrease in the diffusion coefficient over time, a trend that is also supported by the experimental results.

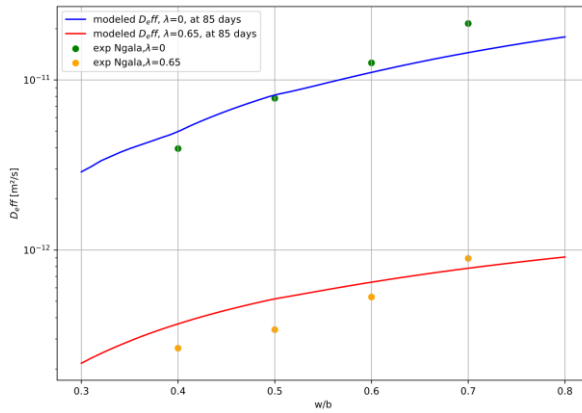


Figure 97: Evolution of the effective diffusion coefficient to w/b, for experimental data by Ngala [292] ($\lambda=0$ and 0.65).

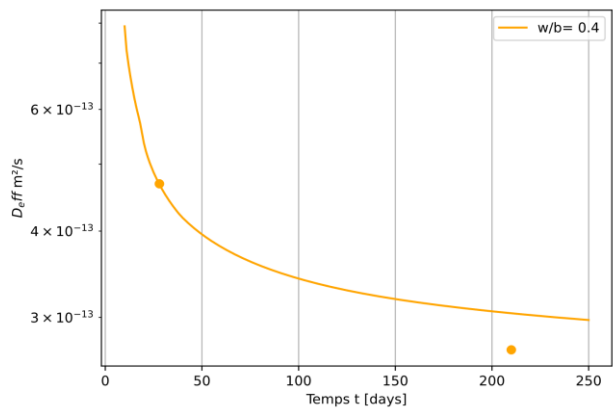


Figure 98: Evolution of the effective diffusion coefficient through time, for experimental data by Wilson [301] ($\lambda=0.5$ and $w/b=0.4$).

Another parameter that has to be considered regarding the evolution of the diffusion coefficient over time is the slag substitution rate. Figure 99 presents the modeled diffusion coefficient vs. experimental data from McNally & Sheils [308] after a curing period of 90 days, highlighting several key points:

- The model reliably predicts the diffusion coefficient across different experimental conditions.
- It accurately reflects the changes in diffusion coefficient with varying water-to-cement ratios, showing that a lower water-to-cement ratio leads to a decreased diffusion coefficient.
- The model also effectively incorporates the impact of slag substitution, showing that an increase in slag content leads to a significant reduction in the diffusion coefficient. This finding aligns with the initial hypothesis and objective of this study, confirming that adding slag to cement markedly decreases the diffusion coefficient of the paste, though the relationship is not strictly linear - since increasing the slag content slows down the rate of hydration, increasing the slag substitution rate

beyond 0.6 can be slightly detrimental on D_{eff} as seen in Figure 99. However, at later ages, this limit on lambda might raise.

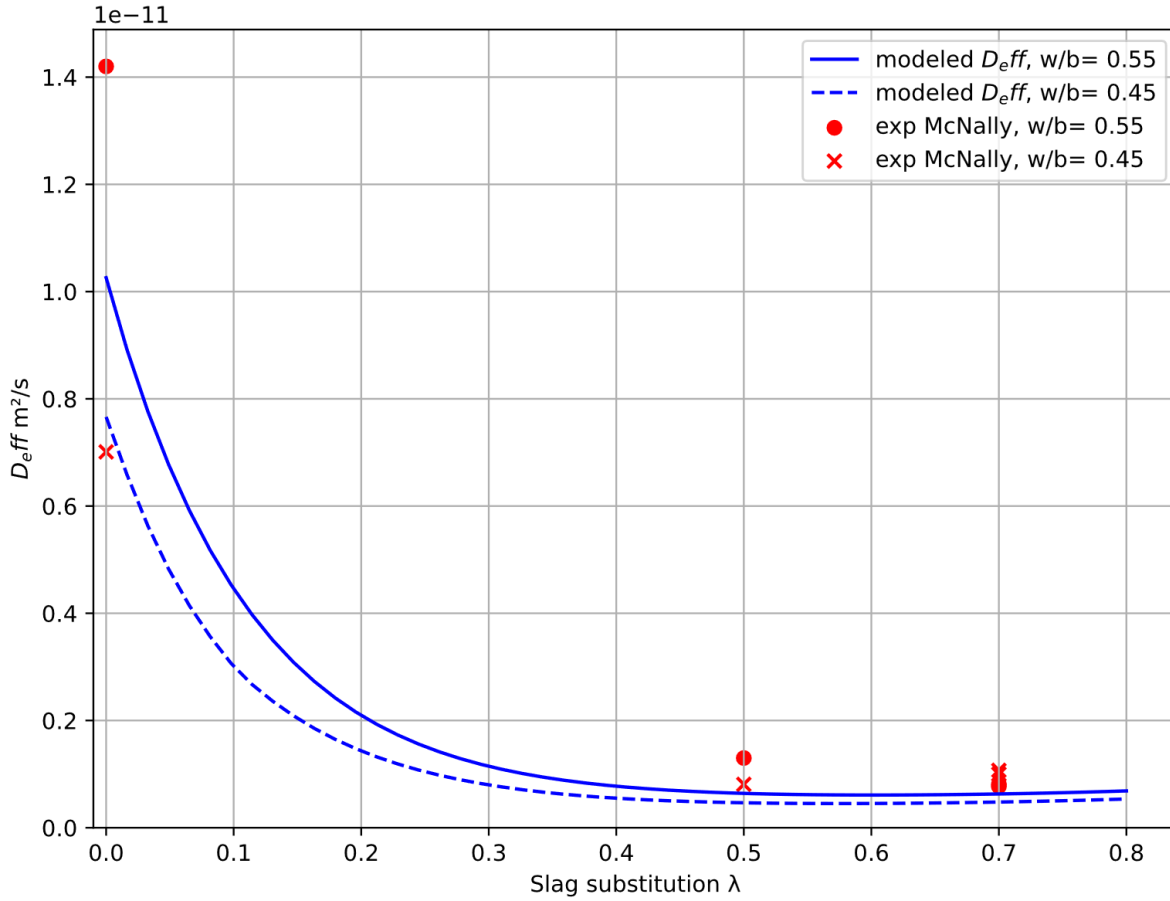


Figure 99: Evolution of the effective diffusion coefficient to slag substitution λ , for experimentally data provided by McNally & Sheils after a curing period of 90 days [308] ($w/b=0.45$ and 0.55 ; $\lambda=0, 0.5$ and 0.7).

VII.4- Conclusion

The extended model (1), developed using a continuum micromechanics approach, successfully integrates detailed morphological models and homogenization schemes to model the diffusion properties of slag-blended cement pastes. By employing a comprehensive multi-scale modeling strategy, using the Mori-Tanaka scheme to upscale from the hydrate foam level to the paste level, the model accurately captures the complex interactions between solid and porous phases, specifically focusing on the distinction between calcium silicate hydrate (C-S-A-H) and other crystalline hydrates.

A comparative analysis of models incorporating various alternative hypotheses, such as using the self-consistent scheme to upscale from the hydrate foam level to the paste level or considering a distinction in

capillary porosity, demonstrated favorable statistical performance when compared to the developed model for CEM I pastes. This highlights potential areas for improvement, applying the same methodologies for slag substitution on these models in order to obtain other well-performing models.

Through rigorous validation against experimental data, the model demonstrates robust predictive capabilities ($R^2=0.77$ for the overall database P_{all} on 70 data points). The incorporation of slag into the cement paste significantly alters the microstructure and transport properties of C-S-A-H gel, resulting in a noticeable decrease in its diffusion coefficient. The extended 2 scale diffusion model, which distinguishes between crystalline and porous hydrates, aligns closely with empirical observations, offering a possible realistic representation of the material.

Key findings include the model's ability to:

- Model the diffusion coefficient of slag blended cement pastes, validated against diverse experimental conditions such as water to binder ratio.
- Highlight the impact of slag substitution on microstructural evolution and diffusion properties through time, emphasizing changes in porosity and phase composition.

This model not only enhances our understanding of the microstructural changes induced by slag substitution but also provides a reliable tool for predicting the performance of slag-blended cement pastes. Its ability to account for varying hydration times, water-to-cement ratios, and slag substitution levels ensures its applicability across a wide range of conditions, thereby contributing valuable insights into the durability and long-term performance of these materials.

This model can serve as an effective tool for optimizing the amount of slag to be added to the cement mix to minimize diffusion coefficients. By incorporating a broad range of mixing parameters—such as temperature, water content, the chemical composition of both the cement and slag among others—it offers a versatile framework for adjusting the cement mix design to achieve enhanced performance, particularly in terms of diffusion in various environmental conditions.

Chapter VIII

Conclusion and Perspectives

The model detailed in this thesis provides an investigation into the hydration and diffusion coefficient of slag-blended cementitious materials, for an application to concrete structures exposed to marine environments. The developed hydration model captures the evolution of hydration phases and porosity through time. These outputs serve as input parameters for the multi-scale model, which provides the effective diffusion coefficient for slag-blended cement pastes. This research contributes to the DEMCOM project, by providing an analytical, fast computationally prediction model for diffusion coefficients in slag-blended cementitious materials. These results are used for coupling with Life Cycle Assessment (LCA) and Life Cycle Costing (LCC) analyses, as it utilizes the same input parameters from slag blended concrete mixtures.

The two-scale diffusion model developed effectively captures the impact of slag substitution on the microstructure, which in turn influences the diffusion coefficient. The diffusion coefficient decrease non-linearly with increasing slag content, therefore, the developed model provides a valuable tool for predicting the diffusion properties of slag-blended systems under long-term exposure to marine environments. This model is a result of a 2 part compilation: a hydration model (a compilation (Chapter IV) of hydration mechanisms (Chapter II) with kinetic terms (Chapter III)) and a multi-scale model (Chapter VII) (taking into consideration the observed microstructure (Chapter V) and validated using an extensive diffusion database compiled from literature (Chapter VI)).

VIII.1- Conclusion

The key conclusions drawn from the studies in Chapters II, III, and IV are presented first.

One of the key aspects addressed in this research is the development of a hydration model specifically dedicated to slag-blended cements. For that purpose, a detailed extensive literature review was conducted to evaluate and benchmark existing hydration models. The primary goal was to develop the most optimal model for slag blended cement hydration that balances both reliability in predicting complex hydration behaviors and analytical simplicity to ensure efficient computational performance for large-scale simulations. This model also captures the kinetics of both clinker and slag hydration in blended systems.

The benchmarking process of existing hydration models involved a thorough comparison of various models proposed in literature, focusing on each model's advantages and limitations. This benchmarking process for the hydration models involved comparing their predictions with experimental data from different studies. These studies included data on the hydration of pure clinker systems, as well as blended systems with varying proportions of slag. Several key metrics were used for comparison, including the evolution of phases' volume fractions, and the formation of hydration products such as portlandite (CH). The literature review revealed that while most models provide reasonable predictions for Ordinary Portland Cement (OPC), fewer models adequately capture the hydration behavior of slag-blended systems. This gap in the literature highlights the need for a concise analytical model, optimized for rapid execution to facilitate integration with Life Cycle Assessment (LCA) tools for slag blended cementitious materials.

As slag has a slower and more complex hydration process compared to clinker, these models must integrate both the chemical and kinetic aspects of hydration to provide accurate predictions over time.

To address the physico-chemical processes involved in slag-blended cements hydration, this research adopted the chemical model proposed by Chen & Brouwers [51, 65, 84] that investigates the stoichiometric effects of clinker and slag hydration on the C-S-A-H phase, particularly the C/S and A/S ratios, which vary with slag content. This model, that is based on the incorporation of partial portlandite involvement in slag hydration, suggest that increasing slag content decreases the C/S ratio while increasing the A/S ratio. This model was chosen because of its ability to accurately describe the hydration products formed in systems containing slag.

The chemical model did not however, describe the time-dependent evolution of hydration. Therefore, it was necessary to couple it with a kinetic model to account for the evolution of the hydration process in function of hydration time. This model treated the kinetics of clinker and slag hydration as separate processes. After evaluating several kinetic models, the clinker kinetic model proposed by Bernard [10] was selected for its robustness and accuracy in predicting the hydration rates of clinker phases. This model is based on a three process framework, which considers the dissolution of clinker phases, nucleation and growth mechanism and the diffusion-controlled hydration.

For the slag hydration kinetic, however, a different approach was needed due to the limitations of slag kinetics model found in the literature. A new kinetic model for slag hydration was proposed, which was based on a comprehensive dataset gathered from various experimental studies in the literature. This dataset includes data from long-term hydration studies, which provided insights into the continued hydration of slag over extended periods. This is particularly important for predicting the long-term durability of slag-blended systems, as slag continues to hydrate for years after the initial mixing. This dataset included also information on the hydration rates of slag at different temperatures, water-to-binder ratios, and slag substitution levels. The model's ability to predict this long-term hydration behavior is one of its key strengths, along with its sensitivity to various parameters (such as chemical composition of clinker and slag, their fineness, the proportion of reactive slag...) that influence the slag kinetics. The water-to-binder ratio and slag substitution ratio plays a critical role in slag hydration kinetics, influencing both the availability of water and the resulting porosity, which impacts hydration rates and long-term durability and diffusion characteristics. Integrating a kinetic model for slag hydration that encompasses all relevant parameters without relying on empirical data or experimental results addresses a significant gap identified in the literature.

One of the key innovations of this research is the coupling of these chemical and kinetic models, allowing for a more comprehensive description of the hydration process in slag-blended systems through time. By integrating the chemical reactions with the kinetic model of clinker and the developed framework for predicting the slag hydration kinetic [153], the model can capture both the chemical and time-dependent aspects of hydration, providing the time-evolution of the developed phases through the hydration process.

The coupled model was validated using a dataset compiled from the literature, which included data on the hydration of both pure clinker and slag-blended systems with different water-to-cement ratios and slag substitution levels, at different periods. The model's predictions were compared with experimental measurements of the hydration product portlandite, the porosity evolution, and phases' volume fractions over time. The model showed good agreement with the experimental data, demonstrating its ability to accurately predict the hydration process in both pure and blended systems.

The developed hydration model has significant importance in providing the time evolution of the phases' quantities, a key parameter further used in the development of the multi-scale diffusion model.

The main conclusions of the approach used in developing this multi-scale diffusion model detailed in Chapters IV, V and VI are outlined in the following paragraphs.

The multiscale homogenization framework adopted in this study offers a comprehensive approach to modeling the effective diffusion coefficient of cementitious materials. By analyzing the material's microstructure, particularly C-S-H, across the micro and nano scales, the model effectively captures the evolution of diffusivity during slag blended cement hydration.

A central contribution of this work is the development of a two-scale diffusion model, at both the micro and nano scales, that integrates the effects of slag substitution into the diffusion behavior of cement pastes. This model, based on a homogenization approach, successfully addresses the challenges associated with multiscale transport properties by considering the microstructural evolution of the material over time.

The model utilizes different homogenization techniques, particularly Mori-Tanaka (MT) approaches, to upscale properties from the microscopic level to the macroscopic level. This is crucial for accurately representing the diffusion behavior across different scales of cement-based materials.

Furthermore, the diffusion model developed in this research are underpinned by extensive data gathered from the literature. They take into account the mixture composition of clinker and supplementary cementitious materials. These models have been validated against a wide range of experimental datasets (70 data points), including changes in water-to-binder ratios and different slag substitution levels, ensuring their reliability and applicability in real-world scenarios.

To ensure the validity of the developed model, a series of comparative analyses were conducted against experimental data. The results were consistent with experimental observations across various conditions, including different slag substitution rates and water-to-binder ratios.

The model could replicate the trend of increased diffusion with higher water-to-binder ratios, a key factor in the material's long-term durability. This relationship is well supported by experimental evidence and aligns with the physical understanding that higher water content leads to increased capillary porosity, facilitating the transport of aggressive ions. Another crucial aspect of the model's validation was its ability to predict the diffusion behavior of slag-blended systems under different slag content. Experimental data

showed a strong correlation with the model's predictions, confirming that the inclusion of slag reduces the diffusion coefficient, particularly at higher substitution rates.

In summary, the analytical computational model developed in this study effectively reproduces the long-term evolution of hydrated phases. It also calculates the effective diffusion coefficient over time, considering various slag substitution rates and other mixture parameters.

VIII.2- Perspectives

The hydration model developed in this research represents a significant advancement in the understanding of slag-blended cementitious systems. However, the C-S-(A)-H gel effective diffusion coefficient used in the current model were relatively empirical, relying heavily on the diffusion database collected from the literature. A deeper understanding is needed to explain the precise mechanisms and evolution of C-S-A-H porosity with varying slag substitution rates. This can be explored through experimental observations of C-S-A-H under different conditions and slag substitution rates, as well as numerical molecular dynamics simulations. Moreover, slag substitution also influences the composition of the pore solution, which could potentially have significant effects on ionic diffusion that need to be explored further.

The results of this study open several avenues for future research in the field of cementitious materials. One potential direction is the further refinement of the multiscale homogenization approach, particularly by incorporating more detailed characterizations of the material's microstructure. For instance, future models could consider the role of interfacial transition zones (ITZ) between the cement paste and aggregates, which have been shown to influence the transport properties of concrete at larger scales.

The next phase of this work aligns with the goals set out by the DEMCOM project, aiming to extend the developed models to the scale of concrete to predict its diffusion properties. The same methodology can be furthermore considered to determine the resistivity and permeability of cementitious structures, exploring their correlation with experimental results obtained with non-destructive methods explored in the DEMCOM project. In addition to extending this model to other transfer properties, this research aligns with the broader objectives of the DEMCOM project, which aims to assess the sustainability and cost-efficiency of cement-based materials. The next phase of the DEMCOM project will leverage the developed multi-scale diffusion model in a multidisciplinary framework for Life Cycle Assessment (LCA) and Life Cycle Cost (LCC) analysis. This will provide insights into optimizing concrete compositions for specific applications, a task of growing importance in the civil engineering and construction industries. The computational efficiency of the model, which was a critical consideration during its development, will play a key role in ensuring the practicality of these large-scale analyses. Ultimately, this approach seeks to identify optimal concrete mixtures that balance durability, performance, and environmental impact, contributing to the development of sustainable construction materials. Moreover, concerning the diffusion model, by providing a reliable predictive tool for assessing the effective diffusion coefficient of slag-blended cementitious systems, this research contributes to the broader field of concrete durability. The two-scale diffusion model developed here can be applied to optimize mix designs, ensuring that concrete

structures achieve the necessary resistance to chloride ingress and other forms of environmental degradation.

The multi-scale methodology presented in this thesis, while primarily focused on the diffusion properties of slag-blended cement, holds significant potential for broader applications in analyzing other transport properties, such as electrical conductivity and resistivity. The robust multi-scale model and homogenization techniques developed in this work can be adapted by modifying the relevant parameters to account for the different transport mechanisms involved in electrical phenomena. These studies would require extensive validation against experimental data, ensuring their reliability and accuracy in predicting both physical and electrochemical behaviors in cementitious systems.

Further promising directions include investigating an extension of the developed model that allows the prediction of sorption and desorption isotherms for slag-blended cements. Additionally, developing fixation isotherms will help refine predictions about ion retention, contributing to a more accurate evaluation of the porous medium's transfer properties. These advancements will also complement the exploration of how ionic composition in the pore solution affects hydration kinetics and diffusion properties—an aspect we have identified but not explored in depth in this study.

Furthermore, the research emphasizes the importance of continued investigation into the long-term behavior of slag-blended cements. While the developed model provides a robust framework for predicting diffusion behavior, future studies could expand on this work by exploring the effects of additional supplementary cementitious materials, as well as the influence of varying mixture parameters. The incorporation of real-world data into these models will be crucial in refining their predictive capabilities and ensuring their applicability to a wide range of concrete applications. A key area of future work lies in modeling under non-saturated conditions, which will allow for a more realistic prediction of the material's behavior under varying environmental conditions. The introduction of partial saturation models will offer a more comprehensive understanding of the system's response to changes in moisture content.

One potential area for future research is the incorporation of additional supplementary cementitious materials, such as fly ash, silica fume and calcined clay into the model. These materials have different hydration behaviors compared to slag, and their interactions with clinker need to be better understood to accurately predict the hydration process in more complex blended systems. Another area for future research is the investigation of the effects of varying mixture parameters on the hydration process. Expanding the model to account for these factors could significantly enhance its predictive accuracy and broaden its applicability to a wider range of concrete structures.

In conclusion, this research provides a comprehensive analysis of the diffusion mechanisms in slag-blended cementitious materials, offering valuable insights into their microstructural evolution and transport properties. The developed two-scale diffusion model represents a significant advancement in the field, providing a reliable tool for predicting the long-term durability of these materials in aggressive environments. Through extensive validation against experimental data, the model has proven to be both

accurate and adaptable, offering a promising foundation for future research and practical applications in the design of durable concrete structures.

Appendix A: Slag hydration degree from literature

Series #	Time (days)	γ	Series #	Time (days)	γ	Series #	Time (days)	γ	Series #	Time (days)	γ	Series #	Time (days)	γ
1	3	6.41	11	3	5.77	20	400	71.92	34	89	53.56	48	183	38.97
1	15	17.24	11	7	11.53	20	795	74.5	34	180	58.56	48	729	43.95
1	30	23.66	11	15	16.84	21	29	32.56	34	363	59.41	49	29	43.52
1	93	30.69	11	29	23.17	21	96	49.09	34	728	62.18	49	91	47.79
1	183	32.83	11	93	34.96	21	196	57.46	35	179	48.42	49	180	50.69
2	3	7.52	11	184	36.82	21	393	66.63	35	363	53.91	49	363	53.57
2	15	19.38	12	3	7.16	21	805	72.98	35	729	60.2	49	726	58.6
2	30	28.03	12	7	12.41	22	29	50.81	36	28	43.27	50	27	41.57
2	93	32.31	12	15	18.85	22	96	62.7	36	91	47.52	50	91	44.12
2	187	37.72	12	30	29.04	22	197	67.64	36	180	50.5	50	180	48.71
3	3	8.9	12	93	38.31	22	395	72.08	36	363	53.47	50	364	47.85
3	15	23.76	12	186	41.56	22	805	76.21	36	729	58.61	50	727	51.86
3	30	30.48	13	3	2.24	23	29	36.12	37	28	32.97	51	10	11.42
3	94	36	13	7	2.85	23	97	48.19	37	91	38.56	51	30	24.87
4	3	12.93	13	15	10.34	23	197	56.55	37	181	43.76	51	94	28.93
4	8	25.76	13	28	11.3	23	394	61.09	37	363	43.86	51	121	30.38
4	15	32	13	92	13.18	23	800	64.5	37	728	45.15	51	371	35.66
4	30	37	13	183	17.5	24	29	55.11	38	28	46.9	51	393	36.05
4	94	40.69	14	3	3.81	24	96	62.02	38	182	69.51	52	7	13.76
4	188	41.93	14	7	4.45	24	196	64.91	38	364	76.16	52	92	20.57
5	3	4.84	14	14	11.35	24	394	69.14	39	28	38.72	52	372	24.2
5	8	8.14	14	30	15.04	24	800	71.83	39	183	58.97	53	10	25.29
5	15	14.01	14	91	17.17	25	28	40	39	364	66.16	53	28	34.56
5	30	17.4	14	183	20.22	25	91	47	40	7	25.66	53	92	37.55
5	94	18.43	15	3	5.74	25	365	67	40	28	34.61	53	120	37.21
5	184	22.09	15	7	6.66	26	28	35	40	90	37.66	53	370	42.11
6	3	5.66	15	15	15.77	26	91	44	40	119	37.41	53	392	38.97
6	7	12.56	15	30	16.46	26	365	59	40	370	42.23	54	7	20.74
6	15	15.04	15	93	17.83	27	28	32	40	391	39.28	54	92	25.59
6	30	20.96	15	183	20.8	27	91	36	41	7	27.29	55	27	56.29
6	94	28.78	16	3	2.29	27	365	48	41	90	35.15	55	177	71.16
6	186	32.6	16	7	2.59	28	28	43	42	7	11.41	55	359	72.15
7	3	6.44	16	15	10.14	28	365	60	42	28	24.78	56	27	52.92
7	7	11.84	16	28	10.31	29	28	46.06	42	91	28.71	56	180	65.09
7	15	16.99	16	91	12.6	29	91	51.8	42	119	30.38	56	362	67.35
7	30	26.36	16	182	16.21	29	196	54.81	42	370	35.69	57	28	46.42
7	94	31.15	17	3	3.58	29	364	53.71	42	391	35.99	57	91	51.58
7	187	34.6	17	7	4.17	29	728	57.83	43	29	49.27	57	182	55.46
8	3	10.66	17	15	10.44	30	28	42.95	43	92	53.57	57	727	59.31
8	7	15.65	17	29	12.07	30	91	44.96	43	184	58.72	58	27	41.81
8	15	18.64	17	92	14.38	30	196	48.58	43	730	62.01	58	180	64.13
8	30	33	17	183	17.25	30	364	52	44	30	48.08	58	362	72.9
8	93	35.53	18	3	4.19	30	728	54.81	44	367	59.42	59	28	38.58
8	187	35.63	18	7	6.5	31	26	46.29	45	29	46.52	59	181	59.23
9	3	13.8	18	15	11.41	31	89	51.71	45	92	51.77	59	363	66.9
9	8	26.83	18	29	15.88	31	180	55.3	45	183	55.43	60	28	35.12
9	16	32.85	18	93	15.95	31	727	59.27	45	730	58.96	60	363	52.02
9	30	42.53	18	183	17.83	32	27	41.3	46	28	35.22	61	27	37.41
9	96	47.68	19	30	40.18	32	91	43.87	46	364	51.38	61	359	57.11
9	188	50.1	19	97	52.08	32	181	48.38	47	28	33.28	62	28	35.37
10	3	4.33	19	197	57.04	32	727	53.91	47	93	38.74	62	179	47.44
10	7	9.22	19	402	61.71	33	26	30.41	47	183	43.91	62	361	50.25
10	15	14.88	19	800	65.58	33	92	35.99	47	365	43.87	63	28	30.91
10	29	21.47	20	30	55.46	33	182	38.78	47	729	45.14	63	91	36.49
10	92	23.27	20	97	62.3	33	728	43.98	48	28	30.71	63	181	39.26
10	182	25.49	20	197	67.06	34	26	49.41	48	92	36.25	63	727	44.51

Table A-1: Slag hydration degree for all mixtures found in literature at different time.

Appendix B: Differentiation of Porosities

Ma et al. [190] introduced a distinction between inner layer (*IL*) and outer layer (*OL*) hydrates formed during cement hydration. The inner layer comprises hydrates with no internal porosity, while the outer layer consists of outer hydrates (*OH*) and small capillary pores (*SCP*). This relationship can be expressed in terms of volume fractions f as:

$$f_{OL} = f_{OH} + f_{SCP} \quad (\text{B-1})$$

A detailed representation of this conceptual model can be found in Figure B-1.

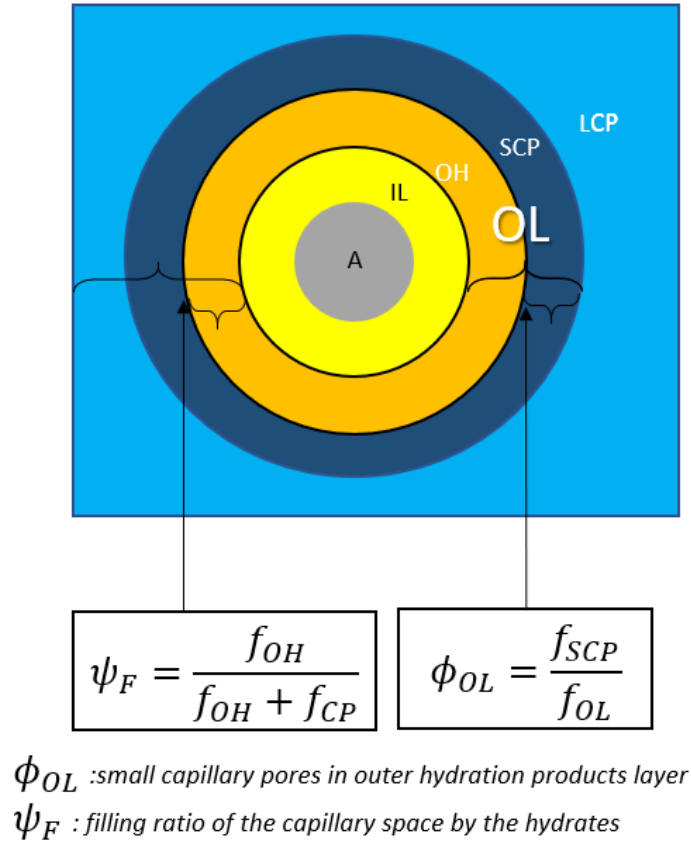


Figure B-1: schematic representation of a hydrated particle.

The porosity of the outer product layer, denoted ϕ_{OL} , is defined as:

$$\phi_{OL} = \frac{f_{SCP}}{f_{OL}} \quad (\text{B-2})$$

Using equations (B-1) and (B-2), f_{SCP} can be reformulated as:

$$f_{SCP} = \frac{\phi_{OL}}{1 - \phi_{OL}} \times f_{OH} \quad (B-3)$$

Additionally, the following expressions apply:

$$f_{OH} = 1 - f_{CP} - f_A - f_{IL} \quad (B-4)$$

Or

$$f_A + f_{IL} = \text{constant} = f_{A0} \quad (B-5)$$

where f_{A0} represents the initial volume fraction of the unhydrated particles. Therefore, we have:

$$f_{OH} = 1 - f_{CP} - f_{A0} \quad (B-6)$$

And

$$f_{SCP} = \frac{\phi_{OL}}{1 - \phi_{OL}} \times (1 - f_{CP} - f_{A0}) \quad (B-7)$$

The parameter ψ_F is defined as the filling ratio of the capillary space by hydrates:

$$\psi_F = \frac{f_{OH}}{f_{OH} + f_{CP}} \quad (B-8)$$

Ma's model suggests that the porosity of the outer product layer, ϕ_{OL} , is linked to the filling ratio of the capillary space by hydrates, ψ_F via the following equation:

$$\phi_{OL} = \phi_{OL}^{initial} (1 - \psi_F) \quad (B-9)$$

By fitting experimental data on CEM I pastes to equation (B-9) as shown in Figure B-2, $\phi_{OL}^{initial} = 0.63$ which is shown to be independent of the water-to-cement w/c.

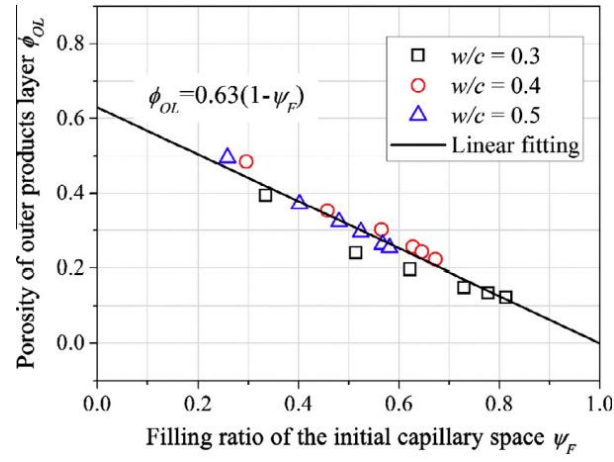


Figure B-2: Linear fitting of the relation between ϕ_{OL} and ψ_F by [190].

In adapting this methodology for slag-blended cements, experimental data from Shanahan et al. [366], Nosouhian et al. [367], Zayed et al. [368], and Ma et al. [369] were employed. These data, obtained through nitrogen adsorption tests corresponding to pore sizes less than 100 nm, cover a range of slag substitution ratios λ (0, 0.3, 0.52, and 0.7), as presented in Figure B-3.

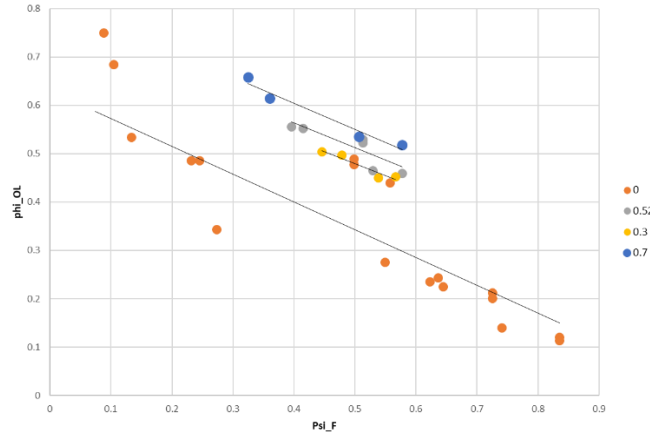


Figure B-3: fitting of the relation between ϕ_{OL} and ψ_F for slag blended cements.

The modified equation for slag-blended systems is:

$$\phi_{OL} = \phi_{OL}^{initial}(1 - \psi_F(1 - 0.84\lambda)) \quad \text{with} \quad \phi_{OL}^{initial} = 0.72. \quad (B-10)$$

With the equations provided, knowing the initial fraction f_{A0} and calculating f_{CP} using the developed hydration model, it is possible to calculate f_{SCP} (equation B-7). This value cannot exceed f_{CP} , in that case, no large pores are present ($f_{SCP} = f_{CP}$). To determine the fraction of large capillary pores f_{LCP} , the computed porosity f_{CP} is subtracted from the small capillary pore fraction f_{SCP} .

Appendix C: Geometrical aspect ratio

Chapter V illustrates the classification of spheroidal shapes based on their aspect ratio (w , defined as the ratio of the axial radius to the transverse radius): oblate, sphere, and prolate.

1. **Oblate ($w < 1$):** Represent a flattened spheroid. Oblate spheroids have an aspect ratio (w) less than 1, meaning they are flattened at the poles and bulge at the equator.
2. **Sphere ($w = 1$):** Represent a perfect sphere. Spheres have an aspect ratio equal to 1, meaning their equatorial and polar diameters are equal.
3. **Prolate ($w > 1$):** Represent an elongated spheroid. Prolate spheroids have an aspect ratio greater than 1, meaning they are elongated along the polar axis.

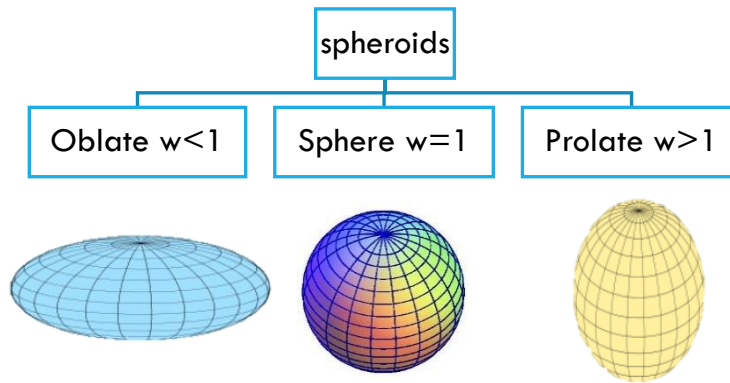


Figure C-1: classification of spheroidal shapes based on aspect ratio.

Appendix D: Statistical Parameters: Definition and Interpretation

In this appendix, we define the statistical parameters used to evaluate the models in the analysis: R^2 , RMSE, MAE, MAPE, SMAPE, and their normalized versions. For each, we describe the objective and target values to optimize model performance.

The coefficient of determination (R^2) measures how well the model explains the variability of the dependent variable based on the independent variables. It is calculated using the equation:

$$R^2 = 1 - \frac{\sum_{i=1}^n (D_{exp,i} - D_{mod,i})^2}{\sum_{i=1}^n (D_{exp,i} - \overline{D_{exp}})^2}$$

where $D_{exp,i}$ and $D_{mod,i}$ represent the experimental and modeled diffusion coefficients for the i -th data point, and $\overline{D_{exp}}$ is the mean of the experimental diffusion coefficients. The closer R^2 is to 1, the better the model fits the data. Since R^2 is dimensionless, higher values are better, with 1 indicating a perfect fit.

Root Mean Square Error (RMSE) quantifies the average magnitude of errors between the experimental and modeled diffusion coefficients, sensitive to larger errors. It is calculated as:

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (D_{exp,i} - D_{mod,i})^2}$$

Smaller values of RMSE are preferable, as they indicate a closer match between experimental and modeled data.

Mean Absolute Error (MAE) provides the average magnitude of absolute errors between the experimental and modeled diffusion coefficients, without the sensitivity to large outliers seen in RMSE. The formula is:

$$MAE = \frac{1}{n} \sum_{i=1}^n |D_{exp,i} - D_{mod,i}|$$

Like RMSE, smaller values indicate better accuracy, so smaller is better for MAE as well.

Mean Absolute Percentage Error (MAPE) expresses the prediction errors as a percentage, making it a scale-independent error metric. It is given by:

$$MAPE = \frac{100\%}{n} \sum_{i=1}^n \left| \frac{D_{exp,i} - D_{mod,i}}{D_{exp,i}} \right|$$

MAPE provides insight into the relative error between experimental and modeled diffusion coefficients. Smaller MAPE values are preferable, and it is expressed as a percentage, meaning smaller values (close to 0%) are better.

Symmetric Mean Absolute Percentage Error (SMAPE) is a more robust relative error metric, defined as:

$$SMAPE = \frac{100\%}{n} \sum_{i=1}^n \frac{|D_{exp,i} - D_{mod,i}|}{\frac{|D_{exp,i}| + |D_{mod,i}|}{2}}$$

SMAPE is less sensitive to extreme values than MAPE, and it is also expressed as a percentage. Smaller SMAPE values are better, and values near 0% indicate high model accuracy.

Normalized RMSE and MAE are versions of RMSE and MAE that are normalized to enable comparisons across different datasets or diffusion ranges. For instance, normalized RMSE (nRMSE) can be computed as:

$$nRMSE = \frac{RMSE}{range\ of\ D_{exp}} \quad \text{and} \quad nMAE = \frac{MAE}{range\ of\ D_{exp}}$$

These normalized metrics are dimensionless and help assess performance across datasets with different scales. As with their unnormalized versions, smaller values are better for nRMSE and normalized MAE (nMAE).

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Titre : Modélisation multi-échelles des propriétés de transport pour l'évaluation de la durabilité du béton armé en milieu marin

Mots clés : Béton; laitiers; Modélisation multi-échelles; Hydratation; Porosité; Diffusion des chlorures

Résumé : La pénétration des chlorures constitue l'une des agressions affectant la durabilité des structures en béton armé, notamment en milieu marin où l'exposition cyclique à l'eau de mer intensifie la pénétration des ions chlorure. Lorsque ces ions atteignent les armatures du béton, ils en provoquent l'oxydation, entraînant une augmentation de leur volume, causant la fissuration du béton d'enrobage.

La résistance à la pénétration des chlorures est déterminée par le coefficient de diffusion du béton, fortement influencé par sa composition. L'incorporation de laitier de haut fourneau amplifie notablement cette résistance. Cette amélioration est due aux modifications de la chimie d'hydratation et aux changements microstructuraux induits, renforçant ainsi la durabilité globale de la matrice cimentaire. Pour modéliser précisément ce processus, un modèle d'hydratation exhaustif a été développé. Ce modèle analytique intègre la description des réactions chimiques d'hydratation du clinker et du laitier, avec plus particulièrement un nouveau modèle cinétique d'hydratation du laitier. Ce modèle a été validé sur une grande base de données et prédit fidèlement l'évolution des phases d'hydratation au cours du temps.

Dans une seconde partie, une modélisation multi-échelles analytique rapide du coefficient de diffusion, spécifique aux ciments avec laitier est mise en œuvre. Elle comprend une représentation de la morphologie des constituants des matériaux cimentaires à différentes échelles de manière physiquement fiable, s'appuyant sur des hypothèses basées sur des paramètres expérimentaux fonder sur des observations morphologiques expérimentales. Les proportions de ces phases sont alimentées par le modèle d'hydratation qui intègre la substitution du laitier. Le coefficient de diffusion des matériaux cimentaires avec laitiers est déterminé alors en fonction de leur composition initiale et de l'évolution de l'hydratation par des techniques d'homogénéisation en champ moyen. Les hypothèses validées par ce modèle reflètent fidèlement les données physiques observées.

En conclusion, ce modèle analytique décrit fidèlement les changements microstructuraux observés expérimentalement, en tenant compte des véritables variations de nature, de quantité et de morphologie des phases hydratées. Il offre ainsi une prédiction fiable du coefficient de diffusion en s'appuyant sur des hypothèses vérifiées, renforçant la durabilité des structures en béton armé.

Title : Multiscale modelling of transport properties for durability assessment of reinforced concrete in marine environment

Keywords : Concrete; Chloride penetration; Multiscale modelling; Hydration; Slag blended cement

Abstract : Chloride ingress represents one of the most severe threats to the durability of cementitious structures, particularly in marine environments where cyclic exposure to water exacerbates the diffusion of chloride ions. When these ions penetrate the concrete cover and reach the steel reinforcement, they initiate oxidation, leading to an increase in rebar volume that causes cracking and structural deterioration. The resistance of concrete to chloride penetration is quantified by the diffusion coefficient, which is heavily influenced by the composition and supplementary materials used in the cement mix. Notably, the incorporation of blast furnace slag has been shown to significantly enhance the resistance to chloride ingress. This improvement is attributed to the alterations in the hydration chemistry and the resultant microstructural changes induced by the slag, thereby enhancing the overall durability of the cementitious matrix. To accurately model these processes, a comprehensive hydration model was developed.

This model integrates an analytical chemical hydration framework that accounts for slag substitution coupled with a literature-based kinetic model of cement hydration and a database-driven model for slag hydration kinetics. The combined model has been validated and effectively predicts the evolution of hydration products through time.

In addition, a microstructural model was formulated based on experimental morphological observations from literature. These observations facilitated the characterization of the geometrical organization and distribution of phases across various length scales. Analytical homogenization techniques, such as the Mori-Tanaka scheme and the self-consistent scheme, were employed to upscale the macroscopic transfer properties from those of each phase at the microscopic scales in order to determine the diffusion coefficient of the cementitious matrix.