Thesis for the degree of Doctor of Philosophy in Civil and Environmental Engineering

NATURAL LOW-KAOLINITE CLAYS AND VOLCANIC MATERIALS AS SCMS: ACTIVATION, HYDRATION PATHWAYS AND POROSITY EVOLUTION

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The cover image summarizes the thesis by showing heterogenous low-kaolinite clays (left) and volcanic materials (right), their activation-induced structural disruption, and a common hydration framework in which reactive Al together with Si, Mg, and Fe partitions into different hydrate formation and links microstructure to binder performance.

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PREFACE

This thesis is submitted to Chalmers University of Technology in line with the requirements for the degree of PhD. The work entailed in this thesis has been conducted at the Department of Architecture and Civil Engineering, at the Building Materials Group, division of Structural Engineering. The PhD was supervised by Associate Professor Arezou Babaahmadi as the main supervisor, with Dr. Liming Huang and Professor Klaartje de Weerdt as co-supervisors, and Professor Holger Wallbaum as examiner.

The research was primarily funded by the Swedish Research Council Formas through the project *New era for cement replacement materials: Importance of service life design (NewDurCem, Grant No. FR-2020/0008)*. Additional funding was provided by Vinnova (Sweden's Innovation Agency, Grant No. 2021-01053) conducted within the strategic innovation programme InfraSweden2030, jointly supported by Vinnova, Formas, and the Swedish Energy Agency. The output of this thesis contributed to work packages for the project titled *Evolution of pozzolan incorporated concrete: resistance to carbonation (Carbo-crete)*, financed by Family Thomas Foundation, from which substantial experimental analyses for this work were funded. The collective contributions from the funding organisers are gratefully recognized.

This doctoral work assesses the viability of locally available pozzolans as supplementary cementitious materials (SCMs), motivated by the anticipated decline in traditional industrial SCMs such as fly ash and slag due to changing production conditions. In Sweden, this challenge is sharpened by national climate regulations introduced in 2020, which target an 85 % reduction in territorial greenhouse gas emissions by 2045. Cement production is identified as one of the most emission-intensive industrial sectors in the EU, and has therefore become a central focus for emission reduction strategies, reinforced by broader European climate commitments.

Against this background, the thesis investigates natural pozzolans with realistic potential for large-scale application. Considering availability, scalability, industrial accessibility, and relevance to the construction sector, clays and volcanic materials (VMs) were identified as the most promising candidates for investigation. A review of the existing literature indicates that studies on activation–reactivity–performance mechanisms of natural pozzolans have predominantly focused on kaolinite-rich clays, owing to their technical attractiveness (i.e., high reactivity and favorable response to calcination). However, the majority of global clay deposits consist of low- or non-kaolinitic clays. This reveals a mismatch between the focus of mechanistic and viability studies and the materials with the greatest practical utilization potential. Additionally, while VMs are available in vast amounts across the world, studies demonstrate a large scatter in results and understanding of their viability as effective binder materials. This is primarily due to the diversity of mineralogy and their associated effects on reaction mechanisms and binder properties. Consequently, there is a need to broaden scientific understanding to encompass more abundant pozzolans with diverse mineralogies. In particular, greater insight is required into how activation processes influence physico-chemical structures and modify hydration evolution mechanisms which ultimately governs binder design in upscaled applications.

Clays found in Sweden predominantly consist of 2:1 clay minerals and often exhibit mixed mineralogies [1, 2]. These minerals are generally considered to have lower reactivity than kaolinite due to their limited response to activation methods optimized for highly reactive SCMs. As such, they reasonably represent the mineralogical characteristics of globally abundant clay resources and therefore constitute suitable candidates for investigation in this study. In addition, VMs from Iceland, encompassing diverse geological origins, were included as complementary pozzolanic systems that are mineralogically distinct yet collectively represent a significant proportion of global pozzolanic deposits.

This thesis is a *kappa*, which represents a synthesis and connection of individual studies presented across five appended papers (A-E). In summary, papers A and B address systematically investigates the relationship between activation routes, physicochemical changes, disruptions in atomic structure, and reactivity in heterogeneous natural clays. Beyond conventional thermal treatments, a combined thermo-mechanochemical activation route was explored as a novel approach. Paper C extends this framework to volcanic pozzolans, which are mineralogically and geologically diverse and fundamentally distinct from clays. Paper D and E evaluates the performance of high pozzolanic thermo-mechanochemically activated low-kaolinite clay and volcanic materials respectively, in blended form. This is done through studies relating to the evolution of hydration properties and phase assemblage chemistry.

ABSTRACT

This thesis investigates the viability of naturally heterogeneous low-kaolinite clays and volcanic materials as supplementary cementitious materials (SCMs) for low-carbon binders. The work is motivated by the need to reduce clinker content in cement under climate constraints and in view of the declining availability of conventional SCMs such as fly ash and slag. In contrast to the kaolinite-rich clays that dominate much of the literature, the materials studied here are mineralogically complex and more representative of abundant natural aluminosilicate resources. The thesis therefore examines how activation modifies their structure and reactivity, and how these changes govern hydration, aluminium partitioning, strength development, and pore structure evolution in blended cement systems.

The results show that the two pozzolan groups respond differently to activation routes. For the clays, a combined thermo-mechanochemical activation (TA-MCA) was effective in improving pozzolanic reactivity. Compared to conventional TA, it improved reactivity by up to 353% and 127% relative to MCA alone. This was accompanied by increases in amorphization of up to 124% and specific surface areas of up to 374%, together with high atomic-scale Al–Si network disruption. TA-MCA caused reduction of crystalline Al(VI) by 88% compared with TA and by 94% compared with MCA and the strongest broadening of ^{27}Al/^{29}Si resonances. For the volcanic materials, MCA improved reactivity across mineralogically diverse precursors, increasing MR3 reactivity from about 40–60 to 400 J/g SCM. In blended cements, the activated clays produced dense microstructures and strong later-age performance, with binary blends at 20–40 wt.% replacement reaching up to 125 % of ordinary Portland cement (OPC) strength at 56 days and the 30 wt.% blend showing a 42 % reduction in total porosity. Aluminium was found to be incorporated preferentially into C–(A)–S–H rather than predominantly into AFm phases, which promoted pore refinement but limited limestone synergy. The volcanic blends hydrated through a more distributed assemblage involving C–(A)–S–H, AFt, possibly strätlingite, and Mg–Al layered double hydroxide-type phases. Although their strength development was slower, 30 wt.% replacement reached OPC-comparable strength at 56 days, while 40 wt.% replacement still achieved about 92 % of OPC strength. Overall, the thesis highlights the potential of complex heterogeneous natural pozzolans to be viable SCMs if mechanisms of their activation and hydration are adequately understood.

Keywords: Supplementary cementitious materials; low-kaolinite clays; volcanic materials; thermo-mechanochemical activation; pozzolanic reactivity; hydration; aluminium partitioning; pore structure; low-carbon binders

SAMMANFATTNING

Denna avhandling undersöker potentialen hos naturligt heterogena lågkaolinitiska leror och vulkaniska material som alternativa bindemedel (SCM) i bindemedel med låg klimatpåverkan. Arbetet motiveras av behovet att minska klinkerhalten i cement mot bakgrund av klimatkrav samt den minskande tillgången på konventionella SCM, såsom flygaska och slagg. Till skillnad från de kaolinitrika leror som ofta studeras i litteraturen är materialen här mineralogiskt mer komplexa och bättre representerar vanliga naturliga aluminiumsilikatresurser. Avhandlingen undersöker hur aktivering påverkar deras struktur och reaktivitet, samt hur detta styr hydratisering, aluminiumfördelning, hållfasthetsutveckling och porstruktur i cementbundna system.

Resultaten visar att de två puzzolangrupperna kräver olika aktiveringsvägar. För lerorna var en kombinerad termo-mekanokemisk aktivering effektiv för att förbättra den puzzolanska reaktiviteten, med ökningar på upp till 353% jämfört med enbart termisk aktivering och 127% jämfört med enbart mekanokemisk aktivering. Detta skedde tillsammans med en ökning i amorfisering på upp till 124%, en ökning i BET-SSA på upp till 374%, samt en tydlig atomskalig störning i Al–Si-nätverket. TA–MCA gav den största strukturella störningen och reducerade kristallint Al(VI) med 88% jämfört med TA och med 94% jämfört med MCA, och den kraftigaste breddningen av ^{27}Al/^{29}Si-resonanser. För de vulkaniska materialen var enbart mekanokemisk aktivering tillräcklig för att markant förbättra reaktiviteten hos mineralogiskt varierande prekursorer, med en ökning av MR3-reaktiviteten från cirka 40–60 till 400 J/g SCM. I cementblandningar gav de aktiverade lerorna täta mikrostrukturer och god hållfasthetsutveckling vid senare åldrar, där binära blandningar med 20–40 vikt-% ersättning nådde upp till 125 % av hållfastheten hos ordinär Portlandcement (OPC) efter 56 dagar, och där blandningen med 30 vikt-% visade en minskning av den totala porositeten med 42 %. Aluminium visade sig inkorporeras företrädesvis i C–(A)–S–H snarare än huvudsakligen i AFm-faser, vilket bidrog till porförfining men begränsade synergier med kalksten. De vulkaniska blandningarna hydratiserade genom en mer distribuerad fasbildning som omfattade C–(A)–S–H, AFt, möjligen strätlingit och Mg–Al-liknande skiktade dubbelhydroxider. Även om deras hållfasthetsutveckling var långsammare uppnådde 30 vikt% ersättning OPC jämförbar hållfasthet efter 56 dagar, medan 40 vikt-% ersättning fortfarande nådde omkring 92 % av OPCs hållfasthet. Sammantaget visar avhandlingen att heterogena naturliga puzzolaner kan bli användbara SCM när deras aktiveringsbehov och hydratiseringsmekanismer förstås väl.

Nyckelord: cementersättningsmaterial; lågkaolinitiska leror; vulkaniska material; termo-mekanokemisk aktivering; puzzolansk reaktivitet; hydratisering; aluminiumfördelning; porstruktur; bindemedel med låg klimatpåverkan

PUBLICATIONS

[A] Amrita Hazarika, Liming Huang, and Arezou Babaahmadi. “Characterisation, activation, and reactivity of heterogenous natural clays.” In: *Materials and Structures/Mat&iaux et Constructions,* (Apr. 2024). DOI: 10.1617/s11527-024-02335-9.
Won RILEM awards for (i) Outstanding Paper 2024, and (ii) Most Downloaded Paper 2024.

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[C] Amrita Hazarika, Liming Huang, Sigurdur Erlingsson, Klaartje de Weerdt, Ingemar Löfgren, Sahar Iftikhar, and Arezou Babaahmadi. “Characterization, activation and reactivity – A case study of Nordic volcanic materials for application as Supplementary Cementitious Materials.” In: *Case Studies in Construction Materials* 22 (Dec. 2024). ISSN: 22145095. DOI: 10.1016/j.cscm.2024.e04096.

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OTHER CONTRIBUTIONS (NOT INCLUDED IN THESIS)

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[3] Amrita Hazarika, Liming Huang, Luping Tang, and Arezou Babaahmadi. "Monitoring of microstructure and strength of composite binder blended with activated heterogenous clay." In: *The 4th International Conference on Calcined Clay for Sustainable Concrete (ICCCSC 2024), Nanjing, China* (May, 2024).

[4] Amrita Hazarika, Liming Huang, Ingemar Löfgren, Luping Tang, and Arezou Babaahmadi. "Correlation of Hydration and Strength to Microstructure of Binders Blended with Volcanic Materials." In: *78th RILEM Annual Week & RILEM International Conference on Sustainable Materials & Structures: Meeting the major challenges of the 21st century - SMS 2024, Toulouse, France* (August, 2024).

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[6] Amrita Hazarika, Liming Huang, Luping Tang, and Arezou Babaahmadi. "Comparing Conductivity, Migration, and Diffusion - Based Indicators of Chloride Transport in Activated Pozzolanic Systems." In: *The 80th RILEM Week in conjunction with the 3rd RILEM Conference on Advances in Climate-Friendly Construction Technology in Africa (ACCTA), Nairobi, Kenya (Abstract accepted)* (September, 2026).

[7] Amrita Hazarika, Liming Huang, and Arezou Babaahmadi. "Activation, Aluminum Pathways, Performance and Transport Properties of Low-Kaolinite Heterogeneous Clay SCMs." In: *The 17th International Congress on the Chemistry of Cement (ICCC 2027), New Delhi, India (Abstract submitted)* (October, 2027).

[8] Amrita Hazarika, Johan Dalene, Klaartje de Weerdt, Liming Huang, Joao Figueira, Ingemar Löfgren, and Arezou Babaahmadi. "Resolving MgO and Aluminum Pathways in Volcanic Supplementary Cementitious Materials: A Multi-Technique Perspective." In: *The 17th International Congress on the Chemistry of Cement (ICCC 2027), New Delhi, India (Abstract submitted)* (October, 2027).

CONTRIBUTIONS

PAPER A Contributed to conceptualization, methodology, experimental design, data curation, investigation, formal and statistical analyses, and manuscript preparation. All sample preparations and testing for pre-treatment, activation, characterization (XRD,ESEM), and reactivity testing (MR3) were performed by the PhD student at Chalmers University of Technology. The tests for ICP-MS was conducted by ALS Global Piteå, TGA and laser diffraction tests were conducted by personnel at RISE, Borås, and FTIR measurements with help at the Department of Chemistry, Chalmers University of Technology. Quantification of XRD through Rietveld was conducted by co-authors. The PhD student conducted analyses of all experimental data, prepared all figures and plots, and led manuscript writing, editing, and revision following peer review comments in collaboration with the co-authors/supervisors.

PAPER B The PhD student led the work, including conceptualization, methodology, experimental design, data curation, investigation, formal and statistical analyses, and manuscript preparation. Sample preparations for all tests were led and performed by the PhD student. Tests for pre-treatments, activations, MR3, FTIR on natural clays were done by the PhD student. NMR testing on natural clays was contributed by co-author at SwedNMR, Umeå. For montmorilonite clays, the atomic scale modelling, TGA and XRD for the single phase clay are conducted and contributed by collaborators/co-authors from University of the Basque Country. The data analyses, preparation of plots, spectroscopic computations, correlations, and writing including manuscript, formatting, editing, revisions following peer review are being conducted by the PhD student in consultations with co-authors/supervisors.

PAPER C The PhD student led the work, including conceptualization, methodology, experimental design, data curation, investigation, formal and statistical analyses, and manuscript preparation. All sample preparations were led and performed by the PhD student. Tests for pre-treatments, activations, XRD, ESEM, MR3 were done by the PhD student. Tests for ICP-MS was conducted at ALS Global, TGA at RISE, Laser diffraction at VTI, Sweden. Hydration stoppage was conducted by co-authors. All analyses, preparation of plots, computations and correlations, and writing including manuscript, formatting, editing, revisions following all stages of peer review were conducted by the PhD student in consultations with co-authors/supervisors. Geological descriptions for the raw materials were contributed by co-authors.

PAPER D The PhD student led the work, including conceptualization, methodology, experimental design, data curation, investigation, formal and statistical analyses, and manuscript preparation. Sample preparations for all tests were led and performed by the PhD student. Tests for pre-treatments, activations, strength, XRD, TGA, isothermal calorimetry, were done by the PhD student. Tests for ICP-MS was conducted at ALS Global, part of TGA at RISE, MIP at China, NMR by co-author at SwedNMR, Umeå. All analyses, preparation of plots, computations and correlations, and writing including manuscript, formatting, editing, revisions following peer review were conducted by the PhD student in consultations with co-authors/supervisors.

PAPER E The PhD student led the work, including conceptualization, methodology, experimental design, data curation, investigation, formal and statistical analyses, and manuscript preparation. Sample preparations for all tests except SEM-EDS were led and performed by the PhD student. Tests for pre-treatments, activations, strength, XRD, TGA, FTIR were done by the PhD student. Tests for ICP-MS was conducted at ALS Global, MIP at China, NMR by co-author at SwedNMR, Umeå, while sample preparation and data collection for SEM-EDS was conducted by co-authors from NTNU, Norway. All analyses, preparation of plots, computations and correlations, and writing including manuscript, formatting, editing, revisions following peer review were conducted by the PhD student in consultations with co-authors/supervisors.

Before there were many, there was one.

— In honour of **Elena Cornaro Piscopia**
History's first documented woman to receive a PhD (1678)

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Global statistics suggest that if granted the PhD, I will be among the estimated 0.4% of women in the world who hold the degree today. For all that this milestone represents, nothing over the past 2 years compares to how much I have looked forward to writing my acknowledgments. As I finally sit writing my way through the final bits of a remarkable journey, I go through a whirlwind of emotions. I know with all my heart that I have not come this far alone. I have been encouraged, supported, carried and loved by a whole village and it is one of the greatest blessings in my life to thank the people who saw me through to this moment. So I take the liberty of stretching these acknowledgments a little, because a short note would simply not do justice.

To my main supervisor, thank you for being so much more than just that. Arezou has not only been a mentor in helping me reach academic milestones (and there have truly been many achievements to celebrate!), but also a steadfast supporter and counselor when things did not work out, a loud cheerleader when they did, a problem solver, a pillar of strength when I battled with reviewers/editors, and at times also a personal psychologist when I needed one most. I am grateful for being given the space to grow independently but even more grateful that she was available at all possible times for all my odd requests, and believed in my ideas (well, mostly!). There was something truly special about being the first student of a new professor, and every highlight of this journey will forever be a core memory. I especially appreciate her for having more or less single-handedly seen us through the storms, which perhaps made our achievements even sweeter. I have way too much to express than what is possible here. Arezou, this has been an honour.

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And so, as I come to the end of this journey, I return to the statistic of 0.4%. If I will stand among that small fraction of women, it is only because I was never standing alone.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACRONYMS

OPC	Ordinary Portland Cement
SCMs	Supplementary Cementitious Materials
GCCA	The Global Cement and Concrete Association
LC3	Limestone Calcined Clay Cements
CCS	Carbon Capture and Storage
VM	Volcanic Materials
CH	Calcium Hydroxide
(M)R3	(Modified) Rapid, Relevant and Reliable (reactivity) test
RQ	Research Questions
TA	Thermal Activation
MCA	Mechanochemical Activation
TA-MCA	Thermo-Mechanochemical Activation
B/P	Ball to Powder Ratio
NC	Nörrköping Clay
SC	Skåne Clay
CC	Calcined Clay
LS	Limestone
PCE	Polycarboxylate Ether
KOH	Potassium Hydroxide
DOA	Degree of Amorphization
LOI	Loss on Ignition
XRD	X-Ray Diffraction
TGA	Thermogravimetric Analysis
PSD	Particle Size Distribution
SSA	Specific Surface Area
BET	Brunauer–Emmett–Teller (test method)
FTIR	Fourier Transform Infrared spectroscopy
ATR-FTIR	Attenuated Total Reflectance-Fourier Transform Infrared
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
SEM	Scanning Electron Microscopy
EDS	Energy-Dispersive X-ray Spectroscopy
MIP	Mercury Intrusion Porosimetry
MAS NMR	Magic Angle Spinning Nuclear Magnetic Resonance

Part I

OVERVIEW

1

INTRODUCTION

1.1 BACKGROUND AND RESEACH CONTEXT

1.1.1 *Cement and its Constraints*

Cement sits in a peculiar category of materials. It is simultaneously ordinary (present in nearly every built environment) and extreme (produced and consumed at a scale that only a few industrial systems can match). Global cement production is currently on the order of 4.1 billion tonnes per year [3] meaning that a material designed to become rock-like within hours is manufactured on a gigatonne scale continuously. This scale is not merely an engineering curiosity but a central feature of contemporary development, because cement-based construction remains the most accessible route to reliable and durable infrastructure across many climates and economic contexts.

A broader lens makes this more striking. In the early 2020s, Earth crossed a symbolic threshold where the mass of human-made materials was estimated to have reached and surpassed the total living biomass, with anthropogenic mass doubling roughly every two decades [4]. Cement-based materials are at the core of that expansion. In this sense, concrete is not merely a construction input but a defining marker of humanity's physical footprint on the planet. At the same time, infrastructure development remains tightly coupled to socioeconomic progress. Emerging economies require sustained investment in housing, transport, water, and energy systems to approach the living standards of high-income nations, and concrete is foundational to this development [5].

The climate problem, however, is that cement production is constrained by chemistry as much as by energy. The conventional clinker production sector is widely recognised as a major contributor to anthropogenic CO_2 emissions, accounting for around 7-8% of global CO_2 emissions on a gross (territorial) basis [6], and roughly 3-4% on a net basis when long-term carbonation uptake is considered [7]. However, decarbonisation is structurally difficult because approximately 60% of these emissions arise directly from the calcination of limestone which is an inherent process emission, while the remainder is largely linked to fuel combustion and electricity use [5, 8, 9]. Because a substantial fraction of emissions is chemically unavoidable under conventional production routes, cement is consistently categorised among the most *hard-to-abate* industrial value chains [10, 11]. Therefore, reconciling the material demands for global development along with biodiversity stability therefore requires systemic innovation not only in energy supply, but primarily in clinker chemistry, material efficiency, and carbon management across the cement–concrete value system.

Against this global backdrop, Sweden provides a relevant case through which to explore these challenges. Like the wider European Union, Sweden operates under stringent, legally binding climate targets that require rapid and deep reductions in greenhouse gas emissions. Sweden's climate policy framework targets net-zero greenhouse gas emissions by 2045 and specifies that emissions from activities within Sweden must be at least 85% lower in 2045 compared with 1990 levels, with remaining reductions achieved through supplementary measures [12, 13]. These legally binding targets mean that sectors like cement and concrete, which are hard to decarbonise, must reduce their emissions much faster than they otherwise would. At the same time, infrastructure in Sweden and the Nordic region faces harsh environmental conditions, especially chloride exposure from seawater and de-icing salts and repeated freeze–thaw cycles [14, 15] . This means emissions must be reduced significantly, but without impairing the durability of concrete. The Swedish and broader Nordic setting therefore serves as a compelling case in which low-carbon binder development must be approached simultaneously as a climate mitigation challenge and as a durability engineering problem.

1.1.2 *Clinker Reduction as a Practical Near-Term Solution*

Multiple decarbonisation levers exist for the cement and concrete system, such as improving kiln efficiency, increasing alternative fuel substitution, deploying carbon capture, improving material efficiency, and reducing the clinker content of cement through supplementary cementitious materials (SCMs). Among these, clinker reduction is often identified as the most deployable near-term strategy because it can be implemented through cement formulation and standards enabled market uptake without waiting for new kiln lines or CO_2 transport and storage networks [16]. In the same spirit, UNEP's eco-efficient cement assessment argues that, over the next 20 to 30 years, greater use of SCMs and more efficient use of clinker in concrete can deliver large emissions reductions while reducing reliance on costly CCS deployment, particularly in regions where affordability and scale are decisive [17]. Lowering clinker directly targets the calcination component, where each percentage point reduction in clinker content reduces the need for limestone decomposition, provided that the substitute material can deliver acceptable performance [18].

At the industry level, there is evidence of progress in emissions intensity. The Global Cement and Concrete Association (GCCA) reports that its 2023 GNR dataset indicates a 25.1% reduction in CO_2 per tonne of cementitious material since 1990 [19]. It notes however that this progress while meaningful, remains insufficient to align the sector with a net-zero trajectory without a much faster scale-up of clinker substitution, along with other pathways. The continued production of billions of tonnes of cement each year means that lowering emissions per tonne is not enough, especially as global infrastructure demand keeps growing and ageing structures need replacement.

Recent research by Hafez et.al.[20] reinforces this conclusion. Their study shows that low-carbon concrete with reduced binder content and upto 50%

clinker replacement can halve embodied emissions at the building level compared to conventional concrete, and could deliver up to 14.3 Gt CO_2(eq.) in cumulative savings globally by 2050. Unlike bio-based structural alternatives, which are constrained by limited forest resources, low-clinker cement pathways are not fundamentally resource-limited and are better aligned with projected urban growth. In that context, SCMs remain central as the most practical and economical way to reduce clinker dependance at scale in the 2020s.

The implication, therefore, is that the SCM challenge is no longer simply about substitution rates, but also about material availability, performance reliability, and long-term scalability. As traditional SCM streams such as fly ash and slag face regional scarcity and structural decline, the challenge shifts from incremental blending to securing abundant, technically robust alternatives capable of sustaining deep clinker reduction at global scale.

1.1.3 *SCMs Decline and the Emphasis on Natural Pozzolans*

An inherent complication has emerged alongside the decarbonisation of energy and heavy industry. Conventional SCMs have historically relied on industrial by-products, particularly fly ash from coal power industry and slag from blast furnace steel production. Yet the energy transition and industrial restructuring that are necessary for climate goals are also expected to tighten these by-product supply chains while leading to increased prices of available reserves due to heightened demand [17]. A recent EU scenario analysis projects a pronounced decline in the supply of common SCMs over the coming decades. In this work, fly ash supply is predicted to decrease from 8.5 Mt in 2025 to 1.9-2.7 Mt in 2035 and 0-1.1 Mt in 2045, while granulated blast furnace slag supply is predicted to fall from 18-19 Mt in 2025 to 6.9-11.4 Mt in 2035 and 0-3.2 Mt in 2045 [5]. These projections indicate that even if cement demand declines, conventional SCM streams are unlikely to match the long-term demand required to sustain low clinker-to-cement ratios.

This supply crisis is a key reason why the research has shifted towards alternative SCM families with large reserves and wide geographic distribution. However, the functionality of SCMs in Portland-based systems is governed by their ability to contribute reactive oxides, primarily SiO_2, Al_2O_3, and in some cases CaO, that participate in hydration and secondary phase formation. It is emphasised that reactivity depends not simply on total oxide content, but on the presence of reactive aluminosilicate phases capable of interacting with calcium hydroxide and forming C-(A)-S-H or related hydrates [17]. In this context, materials rich in reactive silica and alumina are of particular interest.

Two *natural* SCM families therefore emerge as relevant candidates: calcined clays and volcanic materials (VMs). Clays are attractive because their bulk composition is typically dominated by silica and alumina. It is reported that SiO_2 and Al_2O_3 together commonly exceed 90 wt% in many clay deposits, that highlights their intrinsic chemical suitability [21]. Volcanic materials similarly consist of siliceous or aluminosilicate phases formed under rapid cooling, often exhibiting significant amorphous content and demonstrable pozzolanic activity. They are already used at industrial scale, with global natural pozzolan consumption reported at approximately 75 Mt per year [22]. Importantly, both families exist in large accessible quantities compatible with cement-scale deployment, unlike many industrial by-products [23]. For instance, in Sweden, clay resources occur at considerably large scales. Individual deposits such as the Eriksdal clay field have been reported to exceed 700 million tonnes, indicating that national clay availability is in the hundreds-of-millions-of-tonnes range [1]. Additionally, geological surveys from Norway, Finland and Denmark notes widespread and extensive presence of usable clay resources [24–26]. Additionally, within the wider Nordic region, VM availability is geographically extensive in Iceland. It is reported that Iceland alone generates and mobilises on the order of 30–40 Mt of volcanic particulate material per year, reflecting the scale of volcanic glass–rich resources present in the country [27]. Given the vast availability of both clays and VMs in the greater Nordic region, the current study focuses on the viability and mechanistic assessments of these two pozzolans sourced locally as potential binders.

It must be noted that clay and volcanic SCM resources in the Nordic region are not yet uniformly accessible owing to logistical challenges, limited local processing infrastructure, and climatic constraints, but ongoing industrial and research efforts are progressively reducing these practical barriers and expanding regional feasibility. However, beyond these operational considerations, a more fundamental scientific challenge remains in the implementation of natural pozzolans in both Nordic as well as in a global scale: *heterogeneity*.

Both calcined clays and VMs encompass broad mineralogical and compositional ranges. Consequently, although research activity on these materials has expanded significantly, much of the existing knowledge remains system-specific. Figure 1 shows the research literature published and recorded under the Scopus database. Figure 1(a) shows that from a total of 14,444 papers indexed in Scopus between the years 2000 to 2026 on the topic of clay based cementitious binders, roughly 73% studies have focused on metakaolin or kaolinite-rich clays, which are generally the highest-performing and most predictable systems. However, highly kaolinitic clays are not representative of most natural deposits. As a result, while research activity is concentrated on kaolinite-rich systems, the broader mineralogical spectrum of global clay reserves remains comparatively underexplored, although more research is currently being conducted. This limits the transferable understanding needed for large-scale deployment of clay reserves otherwise available.

Figure 1(b) illustrates the distribution of research on volcanic materials used in cementitious systems, from a total of 3600 papers indexed currently on Scopus on the topic. Volcanic ash and natural pozzolans dominate the field (47.0%), followed by pumice and pumicite (37.1 %). Scoria (6.6 %), basaltic materials (5.0 %), and volcanic tuff (4.3 %) represent comparatively smaller research shares. In contrast to clay-based systems, volcanic material research is distributed across a broader range of geological sources, indicating greater material diversity within this category. This diversity has led to substantial variation in reported performance and in recommended replacement levels. Even within the same nominal VM category, results are often inconsistent across studies, reflecting differences in mineralogy, amorphous content, and testing approaches rather than a uniform material behaviour. This variability creates uncertainty in specifications and limits confident, large-scale implementation.

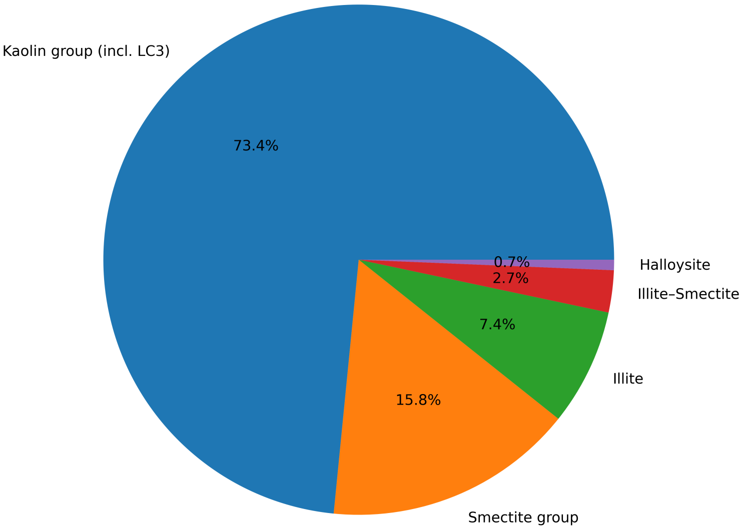
Taken together, the current body of work reflects both opportunity and fragmentation. While calcined clays and volcanic materials are abundant and chemically promising, much of the existing knowledge is derived from specific mineralogical assemblages and cannot be readily extrapolated across the full compositional spectrum within each family. As a result, implementation remains constrained not by availability, but by limited transferability of mechanistic understanding. Fundamental questions therefore persist regarding how mineralogy and oxide chemistry govern activation requirements, hydration pathways, performance development, and durability. Addressing these gaps is essential for translating resource potential into reliable binder design, and forms the basis for the focused investigations presented in the following sections.

1.1.4 *Global Clay Mineralogy and the Limits of Kaolinite-Centric Approaches*

Phyllosilicate clay minerals constitute approximately 21.5 wt % of the Earth's crust [28]. Within this broad mineral family, kaolinite-rich clays have received particular attention in cement research because, upon calcination, they form metakaolin which is a highly reactive aluminosilicate phase suitable for clinker substitution [29–36]. During dehydroxylation, kaolinite transforms into metakaolin, a structurally disordered material that retains some layer stacking but exhibits significant coordination changes, with a portion of octahedral aluminium adopting tetrahedral and pentahedral configurations [37]. Compared with other clay minerals, kaolinite displays a relatively distinct temperature interval between dehydroxylation and recrystallization, which favours the formation of a reactive amorphous phase. When sufficiently pure, metakaolin functions as a highly active SCM, enhancing compressive and flexural strengths as well as durability and resistance to chemical attack [35, 38, 39].

Despite this technical attractiveness, kaolinite-rich clays represent only a fraction of global clay resources. Quantitative estimates summarised by [28] show that illite/mica-type 2:1 clays account for about 7.7 wt% of the crust, smectites about 3.0 wt%, and chlorites (2:1:1) about 5.1 wt%, whereas kaolinite–serpentine (1:1) minerals represent roughly 5.7 wt%. Altogether, 2:1-type clays contribute nearly 16 wt% of the crust, which is almost three times the abundance of kaolinite-rich clays. This disparity is not only quantitative but structurally significant, as mineral structure governs activation behaviour.

Kaolinite, a 1:1 (T–O) clay, possesses near-zero layer charge and layers bonded primarily by hydrogen bonding, leading to a comparatively predictable response to thermal treatment. In contrast, 2:1 (T–O–T) clays carry a permanent negative layer charge arising from isomorphic substitutions, balanced by interlayer cations. This structural feature produces a range of behaviours, from non- or low-expandable illite/mica to highly expandable smectites with hy-



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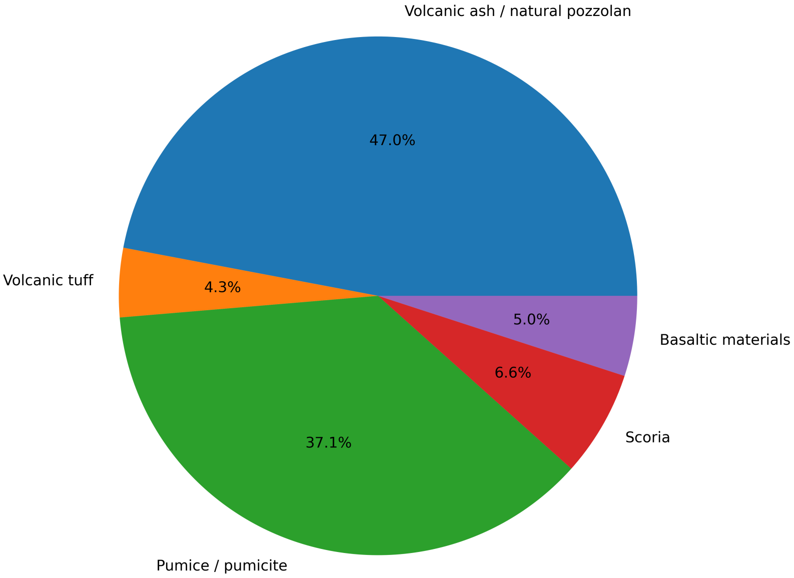


(b)

Figure 1: Distribution of research on (a) clay minerals and (b) volcanic materials used in cementitious systems based on Scopus database. For clays, the classification was made from a total of 14,444 papers, and from 3600 indexed papers for VMs.

drated interlayers [21]. Consequently, the most abundant clay minerals are structurally more complex and may respond differently to calcination than kaolinite. In practical terms, much of cement research has focused on the comparatively well-behaved kaolinite systems, whereas the activation and performance of non-kaolinite clays remain less comprehensively understood.

Economic considerations further complicate this picture. The production of high-purity metakaolin from selected kaolinitic clays has been reported to be up to three times more expensive than Portland cement [40]. Therefore, low-grade or heterogeneous clays which are more abundant and widely distributed, hold greater long-term potential both in terms of resource availability and economic feasibility. Relying exclusively on high-kaolinite systems risks underutilising the broader clay resource base [41].

In response, LC3 technology has demonstrated that calcined clays containing approximately 40 % kaolinite, when combined with limestone, can enable significant clinker substitution through the stabilisation of carboaluminate phases while maintaining mechanical performance [42]. Nevertheless, global mineral distribution patterns suggest that even such 40% kaolinite deposits represent a minority of accessible clay resources. Research by Ito and Wagai [43] show that only highly weathered soil orders such as Oxisols and Ultisols show mean kaolinite fractions exceeding 40–60 % of the clay fraction. Most other soil orders (Alfisols, Inceptisols, Mollisols, Entisols, Aridisols, Vertisols, etc.) show kaolinite fractions typically below 30 %, often below 20 %. Additionally, Lehmann et al. [2] use this dataset to demonstrate that globally, kaolinite-rich soils are largely confined to humid tropical belts, whereas temperate, arid, and high-latitude regions, including Sweden and the broader Nordic region are dominated by 2:1 clays (illite, smectite, chlorite). Collectively, these data indicate that kaolinite-rich deposits are both geographically restricted and mineralogically limited.

This disparity highlights the need to expand research beyond high-kaolinite systems toward the more abundant, yet less understood, heterogeneous clay deposits that ultimately determine the realistic scalability of calcined clay technologies. This thesis focuses on mineralogically realistic materials that are lesser understood in the current context. It is focused on Swedish low-kaolinite clays and addresses the following three gaps:

(i) Exploring the feasible activation conditions that can enable meaningful clinker substitution.

(ii) Clarifying how activation modifies the atomic and short-range structural order of these clays.

(iii) Elucidating their hydration behaviour and reaction pathways, including whether carbonate–aluminate interactions comparable to LC3 systems can be achieved for accomplishing high OPC substitutions.

1.1.5 *Volcanic Materials as SCMs: Variability, Mechanisms, and Implementation Challenges*

Volcanic materials have a long history as natural pozzolans and are permitted within cement standards in many regions [44, 45]. Yet volcanic SCMs vary strongly in glass content, alteration degree and mineral assemblage leading to variations in alumino-silicate contents. As a result, as shown in Figure1 (b), a variety of VM families are recognised as potential SCMs in current literature [46–52]. At the scale of the Earth's surface, volcanic rocks occupy about 6 % of continents and islands [53]. Yet SCM suitability is controlled less by the areal abundance of volcanic rocks but by the fraction of reactive aluminosilicate glass preserved in the deposit. It is reported that the major active component of unaltered pyroclastic pumices and ashes is volcanic aluminosilicate glass that is typically present at more than 50 wt %, while deposits with substantially less glass can be less reactive for instance, with 25 wt % glass [54]. This glass fraction is itself sensitive to alteration (zeolitisation, palagonitisation, argillitisation), which changes the mineral assemblage and therefore, also the effective reactive Al–Si composition.

In parallel, bulk chemistry varies systematically across volcanic materials. While SiO_2 and Al_2O_3 varies across different types of VMs, varying amounts of Fe_2O_3, MgO and CaO are commonly present [54]. Because CaO, MgO, and Fe-oxides can modify glass-network structure, dissolution kinetics, hydrate assemblage, and durability-relevant reactions, their roles are increasingly recognised but still not resolved in a fully transferable mechanistic way across deposits. These compositional variability is one of the main reasons why reported performance in the literature often appears deposit-specific and difficult to generalise. From an SCM transition perspective, the deposit sensitivity is problematic as scaling volcanic SCMs requires activation and binder-design principles that are sufficiently transferable to handle compositional diversity. A clearer mechanistic understanding of how mineralogy and oxide chemistry control performance would enable knowledge to be transferred across similar chemistries, which can support more reliable screening and faster implementation.

Several challenges remain in fully understanding and utilising volcanic materials (VMs) across different geological families. First, many VM groups exhibit relatively low intrinsic reactivity due to heterogeneous mineralogy and complex crystal chemistry [50–52]. While mechanochemical activation (MCA) through intensive grinding has recently shown promise in enhancing reactivity across several VM types, the applied grinding conditions vary widely between studies. Parameters such as grinding time, energy input, and equipment type are often inconsistent, making it difficult to compare results or define optimal activation strategies. In addition, reactivity enhancement is evaluated using different test methods without common benchmarks, which complicates direct comparison, particularly when attempting rapid screening of multiple VM sources.

Second, even for reactive or mechanically activated VMs, most studies focus on macroscopic outcomes such as strength, hydration rate, or durability, often for a single deposit. While these works demonstrate feasible clinker substitution, they seldom clarify the underlying chemical and phase-level mechanisms, particularly in compositionally complex systems. Moreover, volcanic materials are often interpreted by analogy to fly ash or slag, despite distinct chemistries, limiting the development of truly deposit-independent mechanistic frameworks.

In this work, Icelandic volcanic materials are studied because of their relevance to Nordic supply chains and because they provide a strong test case for linking activation-induced changes to binder performance. In particular, the following gaps were outlined to be addressed:

(i) The conditions of mechanochemical activation (MCA) on four mineralogically diverse natural VMs that can improve the reactivity to desirable levels.

(ii) Clarifying the hydration behaviour and reaction pathways of VMs containing varied oxide contents than those typically reported, including whether carbonate–aluminate interactions comparable to LC3 systems can be achieved.

1.2 RESEARCH QUESTIONS (RQS)

The preceding sections identified key gaps related to mineralogical variability, activation strategies, and the limited transferability of current performance frameworks for clays and VMs. To address these gaps, this doctoral work formulates a focused set of research questions aimed at developing both technical processing approaches and mechanistic understanding that can support more generalisable implementation across diverse pozzolanic systems.

The overall objective is to evaluate the viability of locally available Swedish natural and low-kaolinite clays and Icelandic VM as supplementary cementitious materials by systematically linking activation, structure, reactivity, hydration mechanisms and microstructural evolution in blended cement systems. To achieve this aim, the thesis addresses the following specific research questions:

1. Can low-kaolinite clays and mineralogically diverse volcanic materials be effectively activated using common thermal or mechanochemical methods to achieve meaningful pozzolanic reactivity?

2. How do activation techniques modify mineralogy, particle sizes, specific areas and chemical structures of Al-Si networks and how do these changes correlate with measured reactivity?

3. How do activated clays and volcanic materials perform in blended cements in terms of strength and pore structure development relative to OPC?

4. What hydration mechanisms govern these blends, particularly regarding incorporation of aluminium into C-(A)-S-H or AFm phases, and how does this influence synergy with limestone?

5. In MgO Fe_2O_3 containing volcanic SCM systems, how is alumina distributed among C-(A)-S-H, CO_3-AFm phases, Mg and Fe-based hydrates, and how does this partitioning affect mechanical and pore structure evolution?

1.2.1 *Scientific Criteria for Evaluating the Research Questions*

To evaluate the research questions and maintain a consistent scientific basis across the thesis, the following criteria clarify how recurring evaluative terms are interpreted in this work.

- **Effective activation** refers to activation that shifts the SCM from a low-reactive or inert state to a measurably reactive state through coupled structural and physicochemical changes. In the present work, this includes dehydroxylation of clay and VM minerals, reduction of long-range crystallinity, increase in amorphous/disordered content, disruption of Al–Si coordination environments, and physical refinement expressed through lower D50 and/or higher BET specific surface area [33, 37, 55]. These changes are considered effective when they are accompanied by a clear increase in intrinsic reactivity as measured by MR3 calorimetry. In this sense, effective activation is not defined by any single descriptor alone, but by a combined improvement in physical parameters, increase in reactive Al and Si availability together with measurable improvement in MR3 calorimetry test above at least 100-120 J/g SCM [56].
- **Meaningful reactivity** refers to reactivity of SCMs that reaches at least the moderate-reactivity range in MR3/R3-based screening [57, 58] and is sufficient to justify subsequent binder-level investigation beyond low filler-dominated replacement levels [59, 60]. The term is therefore used for SCMs whose reactivity is high enough to support study of hydration, strength development, and pore refinement at replacement levels of at least 30 % and above, rather than only as filler-like additions [57].
- **Meaningful/viable substitution** refers to clinker replacement levels of at least 30 wt.%, since such levels are environmentally relevant and more directly address the need to replace declining conventional SCM streams with abundant alternative resources [17, 23].
- **Viable binder performance** refers to performance demonstrated within the studied binder systems and curing conditions. In this thesis, this means acceptable compressive strength (interpreted against the strength range of common EN 197-1 cements [45], with 32.5 class at 28 days taken as a minimum practical reference). It also includes microstructural refinement at the investigated replacement levels, assessed mainly through hydrate formation and pore refinement relative to OPC and filler reference systems, and interpreted against the performance range of established low-clinker binders such as LC3, CEM II/A-V and CEM II/B-type cements [48, 61–64].
- **Transferability** refers to the extent to which a mechanistic, interpretive, or design framework can be applied across materials with related but non-identical mineralogical and chemical characteristics. This term has been used in existing literature for similar contexts [23, 65, 66]. In this

thesis, it does not imply identical quantitative response, but rather the ability to use the same scientific logic to interpret activation, reactivity, or hydration behavior across compositionally similar natural pozzolans.

- **Mineralogically realistic** refers to materials that reflect the mixed and heterogeneous mineralogy of deposits that are actually available for practical SCM use, rather than idealized end-member materials selected mainly for high purity or high reactivity.

1.2.2 *Mapping RQs to the Appended Papers*

RQs 1 to 2 are addressed by the following appended papers:

- **Paper A:** Establishes activation–structure–reactivity relationships for heterogeneous low-kaolinite clays and demonstrates the effectiveness of TA-MCA.
- **Paper B:** Investigates the atomic-scale origin of activation in heterogeneous clays using FTIR and ^{27}Al/^{29}Si MAS NMR.
- **Paper C:** Demonstrates how mechanochemical activation alters structure and reactivity in Nordic volcanic materials .

RQs 3 to 5 are addressed by the following appended papers:

- **Paper D:** Explains hydration evolution and aluminium uptake pathways in cement blends incorporating activated low-kaolinite clays.
- **Paper E:** Examines hydration development and aluminium distribution in Mg-bearing OPC-volcanic-limestone systems.

The above set of research questions and associated papers can be broadly categorised into three distinct blocks of reactivity, atomic structure and hydration. Figure 2 shows the three blocks and how the research questions are addressed in the appended papers.

1.3 RESEARCH BOUNDARIES AND SCOPE

The following outline the boundaries drawn for the research works, thereby defining the scope of the PhD work:

1. The objective of this study was not to develop new activation methods, but to clarify the correlations governing the pozzolanic potential of clays and VMs as measured by standard reactivity tests such as MR3. The focus was on understanding these relationships within traditionally applied mechanochemical activation (MCA) regimes. Ball milling parameters (ball-to-powder ratio, rotational speed, and duration) were therefore adopted from prior studies that established optimal operating thresholds.

2. For MCA, milling duration was limited to 20 minutes at 500 rpm, consistent with previous findings. Prolonged milling beyond 20 minutes has been reported to promote particle agglomeration and reduce reactivity [55, 67–69]. Extended grinding can also raise mill temperatures above 200 °C, potentially inducing undesirable phase transformations and operational complications [70]. The selected speed of 500 rpm follows recommendations in the cited literature.

3. Only two combined calcination–MCA activation routes were evaluated for the clays, with the aim of achieving at least moderate reactivity suitable for further mechanistic study. The method (TA–MCA20) that was ultimately selected to produce clays for subsequent research points, may not represent the maximum achievable activation but it reflects a practical balance between reactivity gain and energy input. Previous work on Swedish 2:1 clays showed that milling beyond 20 minutes caused significant temperature rise and material caking, reducing milling efficiency [71]. Similarly, [55] reported that extended grinding at 500 rpm and a ball-to-powder ratio of 10 did not improve specific surface area and could even reduce particle refinement. The objective at this stage was therefore not optimisation, but to obtain sufficiently reactive clays for subsequent investigation of hydration and durability mechanisms. In case of VMs, only four MCA durations were tested as again, the goal was to assess how the interlinkages between modified particle sizes, surface areas, amorphous degrees and reactivity evolve. Once they reached moderate reactive levels, further grinding durations were not assessed primarily due to earlier reports of material agglomerations [72].

4. Atomic-scale structural analyses through ^{27}Al/^{29}Si NMR and FTIR were performed on the clay that exhibited the strongest response to activation in Paper A. The objective was to determine how the different activations affected the Al-Si coordination and specifically whether the combined activation treatments induced only surface-level modifications or also produced measurable changes in short-range chemical structure, as reported for other clays subjected to calcination or MCA [73–75]. VMs were not investigated at the atomic scale, as the focus of the study was to evaluate the effect of MCA on reactivity rather than structural transformation. Furthermore, since the studied volcanic materials are already commercially utilized at this stage [76], this thesis primarily aimed to assess measurable changes in their reactivity and to characterize the hydration pathways, particularly examining whether the oxides present in the precursor material influence phase formation.

5. For mixing activated clays for binder designing, a consistent percentage of a tailor made Polycarboxylate Ether (PCE) based superplasticizer was used to deagglomerate and disperse fine clay particles. Efficacy of PCE on the dispersion of varying clay mineralogies has been previously established in notable comprehensive research by [77–80]. As a result, further

detailed analyses into rheology of current activated clays was not prioritised here.

6. Evolution of hydration properties were evaluated at 3, 7, 28, and 56 days. The emphasis was placed on hydration progression and long-term performance rather than early-age reactivity. Papers A and B showed that the activated pozzolans reached medium-reactive pozzolanicity. Previous studies report that even highly reactive metakaolin blends exhibit lower 1-day strength than OPC [38, 81]. Therefore, this study focused on hydration from 3 days onward, when microstructural densification, aluminium incorporation pathways, and strength development become more representative and meaningful. For clay binders, 56 days was selected as the final evaluation point instead of 90 days due to the stepwise experimental design. If significant trends in strength or pore structure evolution had emerged or remained absent at 56 days, extended curing to 90 days would have been considered. Given the large experimental matrix, defining this boundary was necessary to maintain a manageable and logically structured investigation.

7. For the assessment of blend hydration properties, a statistically designed mix proportion matrix was adopted, with SCM additions varied in 10 % increments. This approach enabled efficient coverage of the overall compositional space while maintaining an experimentally manageable number of mixes, and it was not aimed to resolve narrow synergy effects that may arise at smaller replacement levels.

8. Compressive strength and pore structure evolution was monitored on mortars, while hydrate phase characteristics were monitored on pastes. Shrinkage and stress development were not evaluated in this work, as the primary objective was to establish mechanistic links between activation, hydration chemistry, microstructure, and transport performance. Volumetric stability, while important for structural application, represents a system-level response that depends strongly on mixture design and aggregate restraint. It is therefore positioned as a subsequent stage of validation once chemical viability and durability performance have been established.

1.4 THESIS STRUCTURE

The overarching aim of this thesis is to understand the effects of activation on pozzolanic materials, the evolution and characteristics of hydration in their blended systems, and the resulting microstructure of the binders. The thesis is structured in two parts. Part I comprises six chapters that present the framework and investigations, while Part II contains the appended papers.

Following the introduction in Chapter 1, Part I proceeds in a logical sequence: Chapter 2 addresses mineralogical characterisation and activation strategies comprised under the 'Reactivity' and 'Atomic Structure' blocks in Figure

2 and Chapter 3 focuses on blend design and hydration behaviour, categorised under the 'Hydration' block. Chapter 4 presents the main conclusions and limitations, Chapter 5 describes the key developments out of the work entailed in this thesis, and finally Chapter 6 outlines directions for future research.

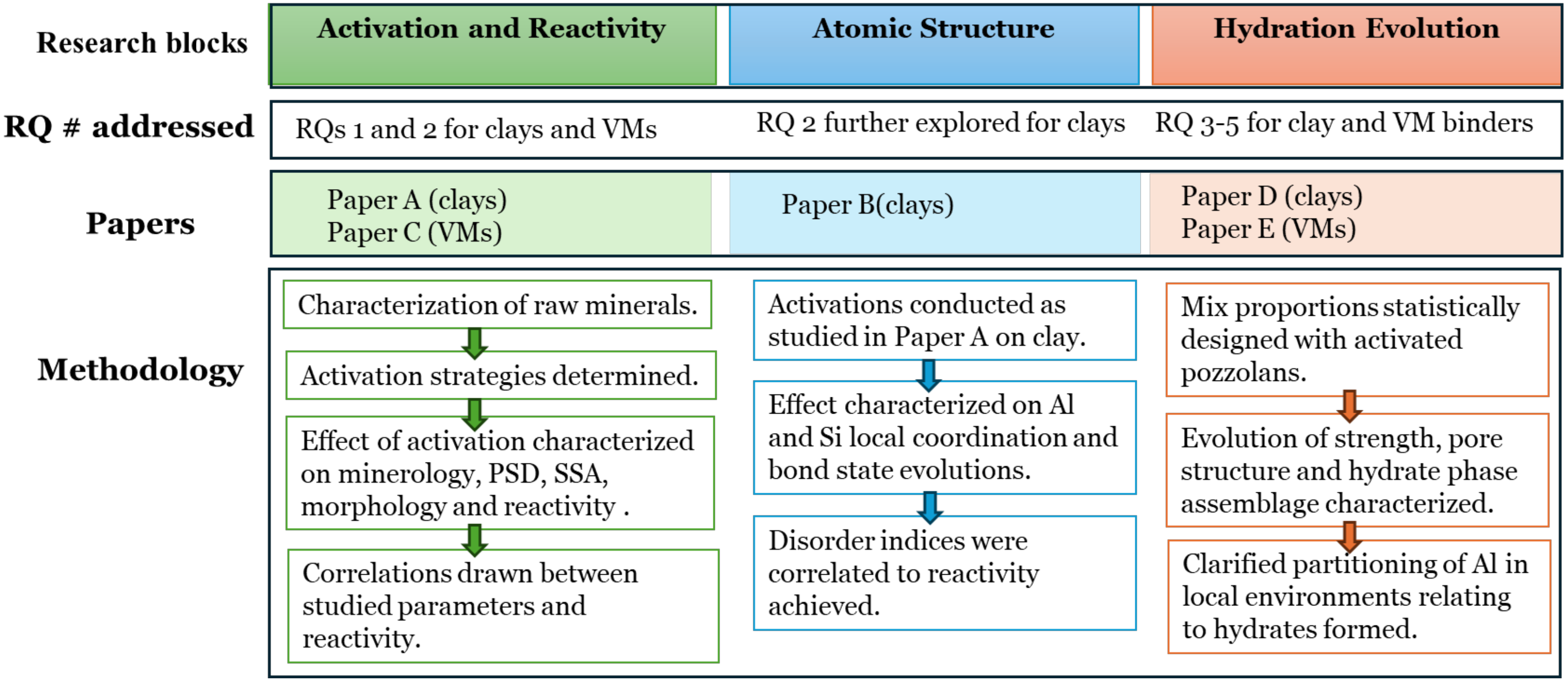


Figure 2: Schematic overview of how the five research questions (RQ1–RQ5) are addressed across the appended papers for clays and VMs. The three blocks of investigations form the research entailed in this thesis.

2

ACTIVATION AND REACTIVITY

This chapter presents the activation processes applied to the clays and volcanic materials investigated in this thesis, and the main findings related to research questions 1 and 2. Based on Papers A, B and C, it establishes the framework through which activation is interpreted in this work and then synthesises the resulting trends in structure, physical properties, and reactivity across both pozzolan families. Detailed material descriptions, experimental procedures, complete datasets, and full analyses are provided in the appended papers, which constitute the primary scientific contributions of this work.

2.1 CONCEPTUAL FRAMEWORK FOR ACTIVATION IN THIS THESIS

In this chapter, activation is approached as the process by which initially low-reactive natural aluminosilicate materials are transformed into precursors capable of participating more effectively in cementitious reactions. In this thesis, the effect of activation is understood through four linked domains: (i) modification of mineralogical order and amorphous content, (ii) disruption of local Al-Si coordination environments, (iii) changes in particle-scale physical characteristics such as particle size distribution and specific surface area, and (iv) the resulting change in measurable intrinsic reactivity. These domains are not assumed to contribute equally in all materials, but together provide the basis for comparing activation effects across different pozzolan families.

This framework is applied here to two materially distinct but practically relevant groups of natural pozzolans: natural low-kaolinite heterogeneous clays and volcanic materials. Although these two groups are not mineralogically equivalent, they are considered together in this chapter because both represent abundant natural SCM resources whose implementation is limited by heterogeneity and by the lack of transferable activation principles. In clays, the reactive fraction is primarily governed by the response of phyllosilicate structures to thermal and mechanochemical treatment [33], whereas in volcanic materials it is governed more strongly by the state of aluminosilicate glass, weakly crystalline phases [54], and deposit-specific oxide chemistry. As a result, the effective activation route is not expected to be universal, although a common interpretive framework can still be used to assess the effect of activation [82].

Accordingly, this chapter examines activation not only in terms of whether reactivity increases, but also through which coupled structural and physical changes such increases are achieved. X-ray diffraction (XRD) is used to assess changes in long-range mineralogical order and amorphization, while Fourier transform infrared spectroscopy (FTIR) and ^{27}Al/^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) are used to examine short-range Al–Si structural disorder where relevant. Particle size distribution (PSD) and Brunauer–Emmett–Teller (BET) surface area measurements are used to quantify physical refinement. Environmental scanning electron microscopy (ESEM) observations of morphological changes are presented in the appended papers. Modified R3 (MR3) calorimetry is used as a comparative screening measure of intrinsic reactivity. Together, these parameters establish the activation-reactivity relationships that define which precursors are later selected for the hydration investigations presented in Chapter 3.

2.2 BACKGROUND OF POZZOLANIC ACTIVATION

2.2.1 *What is Known About Clay Activation?*

Clays, as naturally occurring aluminosilicate minerals in the Earth's crust, exhibit limited intrinsic reactivity in cementitious systems owing to their crystalline structure, low solubility, and thermodynamic stability under alkaline conditions. When incorporated in their untreated form into Portland cement –based binders, their contribution to performance is therefore largely restricted to physical effects, such as particle packing and nucleation, rather than chemical participation in hydration reactions, and is commonly described as a filler effect [83–85]. The deliberate activation of clays to enhance their cementitious or pozzolanic reactivity, however, is not a modern invention. One of the earliest uses of clay in construction was its firing at temperatures approaching 1000 ^{0}C to produce bricks, a technology that constitutes one of the oldest continuously employed building materials in human history [86]. In parallel, archaeological and historical evidence demonstrates that calcined clays and crushed ceramics were intentionally combined with lime to produce hydraulic or pozzolanic binders as early as four millennia ago. Among the oldest, currently well-supported examples are Late Bronze Age mortars from Cyprus (ca. 1200 BCE), where fired clay fragments were deliberately added to lime matrices to enhance strength and durability in the absence of natural pozzolans [87, 88].

A scientific understanding of clay activation began to emerge much later, with the recognition that controlled thermal dehydroxylation of kaolinite at moderate temperatures (typically below 800 °C) yields metakaolin, a highly disordered aluminosilicate phase with pronounced pozzolanic reactivity [33]. This discovery marked a decisive shift away from high-temperature firing toward reactivity-driven calcination, ultimately leading to the acceptance and standardization of calcined clays SCMs. A landmark large-scale application occurred in the 1960s during the construction of the Jupiá hydroelectric reservoir in Brazil, where approximately 300,000 t of locally calcined clay were blended with ordinary Portland cement, demonstrating both the technical feasibility and durability of thermally activated clays in structural concrete [35, 89, 90]. These developments laid the foundation for contemporary research into clay activation. This simultaneously also revealed the limitations of purely thermal approaches, particularly for clay assemblages dominated by non-kaolinitic minerals thereby motivating the exploration of alternative activation strategies.

Thermal activation (TA) is the most established and industrially applied method. Upon heating, clays undergo dehydration at temperatures up to 300 °C, followed by dehydroxylation of structural hydroxyl groups between 300 °C and 800 °C, depending on mineralogy [21, 81, 91]. Dehydroxylation collapses the octahedral sheet, disrupts long-range order, and yields a metastable, partially amorphous phase with enhanced Si and Al dissolution kinetics, which underpins pozzolanic reactivity [33, 35, 92] . This mechanism is well understood for kaolinite-rich clays, where controlled calcination below 800 °C produces highly reactive metakaolin through extensive structural disorder and redistribution of Al coordination [93–96]. Consequently, thermally activated kaolinitic clays have become accepted and standardized SCMs, forming the basis of modern calcined-clay cement systems such as LC3 [42, 61, 97].

In contrast, the effectiveness of thermal activation decreases markedly for heterogeneous, low-kaolinite clays dominated by 2:1 phyllosilicates such as illite, smectite, and mixed illite-smectite. These minerals dehydroxylate over broader and higher temperature ranges, often retain substantial structural order below 900 , and may undergo recrystallisation at elevated temperatures, reducing rather than enhancing reactivity [98]. As a result, purely thermal activation is not a universally viable strategy for the large fraction of natural clays that are mineralogically complex.

To address these limitations, alternative activation routes have been explored. Mechanochemical activation (MCA) via high-energy milling, can induce particle refinement, defect generation, bond rupture, and partial amorphization without the need for elevated temperatures [30, 99–103]. There are various types of milling equipment based on their working principle, such as ball mill, planetary ball mill, attritor or stirring ball mill, vibratory mill, pin mill, rolling mill, and the dry horizontal agitated bead mill [70, 104–106]. The working principles of each of these have been documented in a review by Meng et. al. [21]. Among these, planetary ball mills are the most commonly used and are known for their higher efficiency, precise control over parameters such as ball-to-powder ratio, high rotational speeds, and milling time [107].

In several studies, MCA has been shown to enhance the reactivity of 2:1 clays more effectively than calcination alone [74, 108–112]. At the chemical level, spectroscopic investigations have demonstrated that MCA can also induce substantial disruption of the aluminosilicate framework. Using FTIR and solid-state NMR, Marsh et al. [75] showed that high-energy milling leads to progressive loss of structural hydroxyl signatures, broadening of Si-O stretching bands, and increased disorder in both Al and Si coordination environments, indicative of bond rupture within the octahedral and tetrahedral sheets. These atomic-scale changes have been directly linked to enhanced dissolution kinetics and increased reactivity in alkaline environments. However, despite these advances, much of the mechanistic understanding of mechanochemical activation is still derived from studies on single-phase or synthetic clays, particularly pure kaolinite or montmorillonite, which do not adequately capture the mineralogical complexity, impurity effects, and competing phase responses that are characteristic of natural, multimineral clay assemblages [94]. This limitation has been explicitly highlighted in recent RILEM assessments as a key barrier to the widespread utilisation of natural clays as supplementary cementitious materials [97].

Chemical and physico-chemical approaches, including acid activation [113, 114] and sonication [115], have likewise been investigated in pure 2:1 clay minerals as methods of increasing surface area and porosity or only selectively disrupting octahedral sheets. However, they generally fail to induce deep, bulk structural disorder of the Al-Si framework, which is essential for sustained pozzolanic reactivity in cementitious environments. Besides, achieving meaningful activation requires long sonication times and high energy input, yet the induced structural changes remain shallow compared with MCA or thermal routes. On the other hand, acid and alkaline treatment of clay minerals have many industrial uses but are less common at large scale due to key challenges. These include environmental concerns from acidic waste, the need for careful process optimization, variability in raw clay composition affecting consistency, and added costs from waste treatment. Moreover, the variability of clay minerals can affect the consistency of treatments and make it difficult to maintain uniform treatment at a large scale [21].

Against this framework, the present work explored a combined activation route for two diverse, multi-mineral natural clays by sequencing thermal and mechanochemical treatment. TA–MCA was examined on the premise that the two methods could act complementarily in heterogenous low-kaolinite clays. Thermal activation was expected to first dehydroxylate the more thermally responsive clay fraction, especially the 1:1 minerals, and thereby weaken the overall clay framework. The subsequent MCA step was then expected to more effectively disrupt residual 2:1 phases, refine particle size, generate fresh surface area, promote bond rupture, and increase structural disorder. The sequential route was therefore hypothesised to drive the precursor into a more amorphous and reactive state than either treatment alone, by more effectively disrupting residual ordered domains and exposing additional reactive Al and Si sites. These two activation routes were considered not only because of their expected complementary effects on reactivity, but also because they represent conventional and comparatively feasible processing methods for eventual industrial implementation at larger scale.

To combine the activations, commonly established parameters for TA-MCA were adopted from literature [55, 85, 109, 116] for both TA and MCA parts as further explained in the methods section. The results of TA-MCA on the natural clays was compared against TA and MCA conducted individually on the same clays. The effects were specifically examined on particle size distribution (PSD), specific surface area (SSA), reactivity as measured through cumulative heat of hydration (Modified R3 method [56]), and the structural distortions created in the Al–Si networks post activation, with particular focus on aluminosilicate structural disorder quantified using FTIR and ^{27}Al/^{29}Si

MAS NMR, including spectral deconvolution-based descriptors of Al coordination environments, silicate connectivity, and bond-level disorder that were subsequently related to MR3 reactivity.

2.2.2 *What is Known of VM Activation?*

Volcanic materials have a long history of use as natural pozzolans, most prominently in ancient Roman construction, where volcanic ashes and tuffs were deliberately selected, graded, and combined with lime to produce durable hydraulic binders. Classical sources such as Vitruvius document the preferential use of specific volcanic deposits (e.g. pulvis Puteolanus), indicating an early empirical understanding of reactivity differences among volcanic materials rather than deliberate pre-activation by heat or chemicals. Modern mineralogical investigations of Roman concretes have confirmed that their long-term durability, particularly in marine environments, arose from low-temperature pozzolanic reactions between lime and volcanic glass, and from continued mineral formation (e.g. Al-tobermorite, phillipsite) during service, rather than from any pre-treatment comparable to modern activation methods [88–90]. Nevertheless, many ancient volcanic-based structures did not survive intact, largely due to non-material factors such as seismic damage, foundation failure, weathering, and extensive spoliation, but also because volcanic materials are intrinsically heterogeneous and not uniformly reactive across deposits [117, 118]. With the development and dominance of OPC, the variability that is linked to differences in glass content, crystallinity, and alteration state, rendered volcanic materials less predictable as binders, motivating later efforts to enhance and standardise their reactivity through activation.

Subsequent research has explored thermal, chemical, and mechanical activation routes for volcanic materials, albeit with mixed success. Among the potentially scalable technologies for natural pozzolans, thermal and mechanochemical activation are currently among the most feasible [46, 50, 85]. However, unlike clays, heterogeneous volcanic materials do not undergo a systematic dehydroxylation-driven transformation into a uniformly more reactive phase under thermal activation. Instead, different pyroclastic minerals exhibit markedly different thermal responses and amorphization ranges, while other constituents may simultaneously undergo devitrification, densification, or recrystallization into more stable phases [117, 119, 120]. Previous studies therefore show that the benefit of thermal activation in volcanic materials is often limited and strongly deposit-specific rather than universally beneficial. For example, Liebig and Althaus reported improvement only for suevite at 800,°C and for a phillipsite-rich tuff at 500,°C, whereas Khan et al. found that heating volcanic ash to 550–750,°C reduced amorphous content and pozzolanic reactivity [119, 120]. Together with more recent work by Lemma et al. [121] showing that SCM performance in volcanic precursors is strongly governed by their original glass content and alteration state, these findings indicate that calcination is not a generally transferable activation route for volcanic materials.

Chemical activation, particularly alkaline activation has proven effective for producing geopolymeric binders from volcanic ashes, yet such approaches require high alkali dosages and depart fundamentally from conventional SCM use in Portland cement systems [51, 122]. Consequently, mechanical and mechano chemical activation have emerged as the most widely investigated routes for volcanic materials [68, 69, 123, 124]. High-energy grinding has been repeatedly shown to increase fineness, specific surface area, and internal energy, reduce crystallinity, and partially amorphize volcanic phases, leading to improved dissolution kinetics and enhanced pozzolanic activity [99, 125, 126]. Nevertheless, reported outcomes vary widely due to large differences in milling parameters, and excessive grinding can induce particle agglomeration, limit further reactivity gains, or reduce processing efficiency.

Appended Paper C identified important research gaps in the broader literature on MCA of volcanic materials, particularly the lack of transferable understanding linking milling parameters to the physicochemical variables that govern reactivity across different VM types. Addressing this gap is necessary for developing activation principles that can be applied beyond single deposits and for better utilising the abundant availability of VMs as SCMs.

Accordingly, the present study evaluated four mineralogically diverse and heterogeneous VMs. The objective was to examine how MCA parameters modify the properties that control reactivity in naturally sourced volcanic materials of different composition, age, and geological origin. The activation-induced changes were analysed and quantified in terms of mineralogy, degree of amorphousness, morphology, specific surface area, and reactivity, thereby addressing RQs 1 and 2.

2.2.3 *Background on Reactivity Analyses of SCMs*

The feasibility of new SCMs depends on their pozzolanic or latent hydraulic reactivity, which controls microstructural refinement and long-term durability [23, 127]. Despite extensive research since the last 200 years, no single comprehensive *reactivity* test exists for assessing SCMs rapidly and holistically [82]. Conventional tests developed for Portland cement or traditional SCMs are inadequate for new materials due to slower reaction kinetics and higher variability [128, 129].

The Strength Activity Index (SAI) remains widely used but suffers from major limitations, including neglect of density, mineralogy, oxide distribution, and fineness, often leading to misleading results [130, 131]. Chemical tests such as the Vicat lime consumption test also lack specificity and require long durations, while methods like Frattini and Chapelle show poor reproducibility and limited applicability to heterogeneous SCMs [82, 99, 127, 132, 133]. Alternative conventional tests such as the electrical conductivity tests based on the work by Frattini ignores the fact that not all SCMs require same amount of lime to react and hence may not correlate well with the performance of all pozzolans [99].

To overcome these limitations, the R3 (rapid, robust, relevant) test was developed to simulate cementitious conditions and quantify reactivity through heat release, bound water, and calcium hydroxide consumption, showing strong correlations with compressive strength [82, 133, 134]. It can effectively distinguish inert, pozzolanic, and latent hydraulic materials. The principle behind the reactivity analysis of the R3 tests are based on (i) heat release of an SCM hydrating paste measured by an isothermal calorimeter at 40 degrees for 7 days, or (ii) bound water measurements of the SCM paste between 110 and 400 degrees C after 7 days of curing [128, 133]. While the heat release and bound water measurements enables differentiation between inert and reactive materials, a third test using measurement of calcium hydroxide consumption enables differentiation between pozzolanic and latent hydraulic materials [82]. Significant correlations of reactivity were observed with compressive strength using these R3 tests. Avet et. al.[134] examined the R3 tests on calcined clays with calcined kaolinitic contents > 40 %. They found that both the heat release through isothermal calorimetry, and the bound water determination demonstrate linear correlation to the compressive strength for all ages. They further found linear correlations of these two tests to the modified Chapelle test, indicating that the R3 tests are more practical and closer to reaction conditions in real Portland cement systems.

Despite its advantages, the R3 method was found to have several limitations. A key drawback is that the test is more reflective of early-age reactivity (e.g., 28 days) and may underestimate the long-term performance of slowly reacting materials such as siliceous SCMs (e.g., Class F fly ash), whose reactions continue beyond the test duration [58]. Additionally, the inclusion of sulfates and carbonates can introduce secondary reactions that may not directly correspond to field conditions, complicating interpretation of results [56].

To address these challenges, a *modified* R3 test (MR3) was developed as a simplified and more flexible alternative [56]. Wang et. al. [58] directly compared the R3 and MR3 methods and highlighted key differences in their behavior and applicability. One major limitation of the R3 test is its sensitivity to added sulfates and carbonates, which can artificially increase heat release through secondary reactions, especially in Ca- and Al-rich materials. This can lead to overestimation of reactivity that is not solely attributable to intrinsic SCM behavior. In contrast, the MR3 removes these additions, allowing a clearer assessment of intrinsic pozzolanic or latent hydraulic reactivity. The study also clarified that the R3 test may underestimate the reactivity of slowly reacting siliceous materials (e.g., Class F fly ash), as their reaction does not plateau within the 7-day test duration . The MR3, conducted at higher temperature (50 °C) and longer duration (10 days), better captures this sustained reactivity, producing more representative results for such materials. Furthermore, it was found that although both methods can distinguish inert and reactive materials, the separation is often clearer in the MR3 test, particularly for diverse SCM types [135, 136].

Consequently, in this thesis, MR3 is used as a comparative screening reactivity test for characterizing and classifying the effects of activations on natural heterogenous clays and VMs. Its role is to identify whether activation has meaningfully altered the intrinsic reactivity of the precursor under controlled alkaline conditions, and to enable comparison across materials and activation routes using a common measure. However, MR3 does not by itself resolve the subsequent hydrate assemblage, phase competition, or microstructural development that arise when the activated materials are incorporated into Portland cement systems. For this reason, the reactivity trends established in this chapter are later complemented by hydration-based investigations in Chapter 3.

2.3 MATERIALS AND METHODS OF ACTIVATION AND CHARACTERIZATION

2.3.1 *Pozzolans*

Two natural clays with heterogenous mineralogy were considered for study. The first clay, of glacial type, is sourced from the eastern marine region of Norrköping in Östergötland (labelled here as NC). The second clay in this study is a sedimentary type from the southern region of Ängelholm in Skåne (labelled SC). Both clays have mixed mineralogy consisting of kaolinite, substantial amounts of illite, smectite and some amounts of impurities like quartz. The details are presented in paper A. In case of VMs, to test the activation mechanisms, four types were considered for screening the effect of MCA. The 4 materials were sourced from volcanic deposits surrounding Southern regions of Iceland where these materials are more accessible: Reykjanes Ridge, the Katla central volcano in Mýrdalssandur, Mt. Hekla in Búrfell, and Mt. Litla-Sandfell in Ölfus. These are hereby termed as VM 1-VM 4 respectively. These four types of VMs used for the study are representative of a potentially significant resource for substituting cement in the Nordic region. Paper C describes these VMs more in detail. The oxide composition of the SCMs used are presented in Table 2.

Table 2: Chemical composition (by weight percentage) of the materials

Oxides (wt%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	LOI	Total
NC	51.80	18.35	9.55	1.32	3.34	1.70	8.15	99.86
SC	50.50	15.55	6.70	6.62	2.63	1.36	11.20	99.53
VM 1	48.30	14.60	13.25	11.95	7.44	2.09	-0.52	99.14
VM 2	47.00	12.75	17.15	9.31	4.92	4.92	-0.70	99.71
VM 3	65.60	14.9	7.70	3.62	0.83	4.73	1.44	101.98
VM 4	61.70	14.05	6.04	6.61	2.86	1.88	2.45	100.07

2.3.2 *Treatment and Activation Methods*

Raw pozzolans were first dried at 80 °C to constant mass and pre-ground to obtain a homogeneous powder (<125 μm) prior to activation. Pre-grinding was performed to minimise heterogeneity and ensure uniform activation, as recommended in previous studies [85, 137].

Three activation routes were applied to the clays:

1. **Thermal activation (TA):** Calcination temperature was selected based on thermogravimetric analysis, with dehydroxylation observed below 750–800 °C. Clays were therefore calcined at 800 °C for 60 min to induce structural disorder without recrystallisation, consistent with prior studies [1, 138].

2. **Mechanochemical activation (MCA):** Milling was conducted in a planetary ball mill at 500 rpm with a ball-to-powder ratio of 25 for 20 min, following established parameters for heterogeneous clays [55, 109]. Milling duration was limited to avoid excessive agglomeration and reduction in effective surface area reported at longer grinding times.

3. **Combined activation (TA–MCA):** Thermally activated clays were subsequently subjected to MCA for 10 and 20 min (labelled here as TA–MCA10 and TA–MCA20 respectively) to further disrupt residual 2:1 phases and refine particle size and surface area, with the aim of enhancing reactivity.

From a practical perspective, the selected activation routes also reflect different levels of industrial familiarity and applicability. Thermal activation is already compatible with established calcination technologies and therefore represents the most mature route for scale-up, particularly for clay-based SCM production [85, 139, 140]. MCA, while attractive because it can enhance reactivity without high-temperature treatment, remains more sensitive to milling conditions, energy input, and agglomeration effects, especially for compositionally variable natural materials, and has not yet been fully scaled up for widespread SCM production. Nevertheless, several studies suggest that MCA remains promising, since its average heat demand is much lower than thermal activation (about 208 vs 624 kWh/t), and when powered by renewable electricity it may reduce CO_2 emissions by up to about 70 % on average [21, 85, 141, 142]. The combined TA–MCA route is considered here primarily as a mechanistic and proof-of-viability approach for examining whether low-reactive heterogeneous clays can be driven toward more useful reactive states. Accordingly, the activation programme in this chapter focuses on comparing feasible activation routes and clarifying the governing structure – property – reactivity relationships.

For volcanic materials, thermal activation was not pursued due to mineralogical considerations discussed in Section 2.2.2. Mechanochemical activation was performed under the same milling speed (500 rpm) and ball-to-powder ratio (25) as for clays, with grinding durations varied between 5 and 20 min. Milling time and speed were bounded to avoid excessive agglomeration, ball adherence, and unnecessary energy input, in line with previous studies on natural pozzolans [50, 68–70, 143].

It should be noted that for MCA, an upper milling duration of 20 min was selected based on two considerations. First, earlier studies on heterogeneous clays and natural pozzolans have shown that longer high-energy milling can promote agglomeration, caking, temperature rise, and reduced milling efficiency, without necessarily producing further useful gains in reactivity [55, 67]. Second, the purpose of the activation stage in this thesis was to obtain precursors that were sufficiently reactive for later binder studies at OPC replacement levels beyond the low replacement range typically associated mainly with filler compensation, generally around 10-15 % and at most around 15-20 % [22, 60, 144] depending on the system, rather than to identify a fully optimized milling duration for each material. In this sense, 20 min was treated as a practical upper bound for comparative activation and for reaching at least moderate reactivity suitable for the later hydration-focused investigations.

2.3.3 *Mineral and Structural Characterization*

Mineralogical and structural characterization of the pozzolans was carried out using XRD, FTIR, TGA, and ICP-AES. XRD was used to identify phase assemblages, quantify clay minerals via Rietveld refinement, and assess activation-induced amorphization through degree of crystallinity analysis (formula provided in Paper C). TGA was employed to evaluate dehydroxylation behaviour and mass loss, while ATR-FTIR was used to examine O-H vibrations associated with phyllosilicates and impurities. Detailed experimental procedures are provided in Paper A.

To further examine activation-induced structural distortions, a complementary atomic-scale study was conducted on the clay exhibiting the strongest activation response (Paper B). The evolution of Al and Si coordination under thermal, mechanochemical, and combined TA-MCA treatments was investigated using ^{27}Al and ^{29}Si MAS NMR in conjunction with FTIR. This analysis aimed to determine whether combined activation induced chemical and short-range structural modifications beyond particle size and surface area effects, thereby assessing the mechanistic generalisability of TA-MCA for heterogeneous, low-kaolinite clays. Atomic-scale coordination analysis was not extended to volcanic materials due to their multiphase nature and the resulting complexity of spectral deconvolution, which was beyond the scope of the activation screening study. The relative fractions of Al coordination environments were determined by deconvoluting the ^{27}Al MAS NMR spectra and normalizing the integrated areas of the fitted Al(IV), Al(V), Al(VI), and distorted Al(VI) peaks to the total fitted spectral area.

Bulk oxide compositions were determined by ICP-AES following fusion digestion, and loss on ignition was measured by TGA. Full analytical details are provided in the appended papers.

2.3.4 *Particle Size Distributions, Specific Surface Area and Morphology*

Particle size distributions were determined by laser diffraction (Mastersizer 3000, Malvern Panalytical) following dispersion in water, with ultrasonication applied to minimise agglomeration. Specific surface area was measured using N_2 adsorption (BET method, TriStar 3000). Surface morphology of selected activated volcanic materials was examined using scanning electron microscopy (FEI Quanta 200 FEG). Detailed measurement parameters are provided in the appended papers.

2.3.5 *Reactivity*

Reactivity was evaluated using the modified R3 (MR3) test in an isothermal calorimeter[127]. Although no universal threshold has been standardised [58], literature provides indicative cumulative heat release ranges to classify SCM reactivity [145]. Approximately 100 J/g SCM is commonly used to distinguish inert from reactive materials, 200-600 J/g SCM for mid-reactive clays, 150-400 J/g SCM for moderately reactive pozzolans including volcanic materials, above 600 J/g SCM for highly reactive clays, and above 400 J/g SCM for highly reactive volcanic materials. These category-specific thresholds reflect differences in mineralogy, amorphous content, and reaction kinetics [57, 146]. Accordingly, distinct ranges were adopted in this study to classify the reactivity levels of clays and volcanic materials.

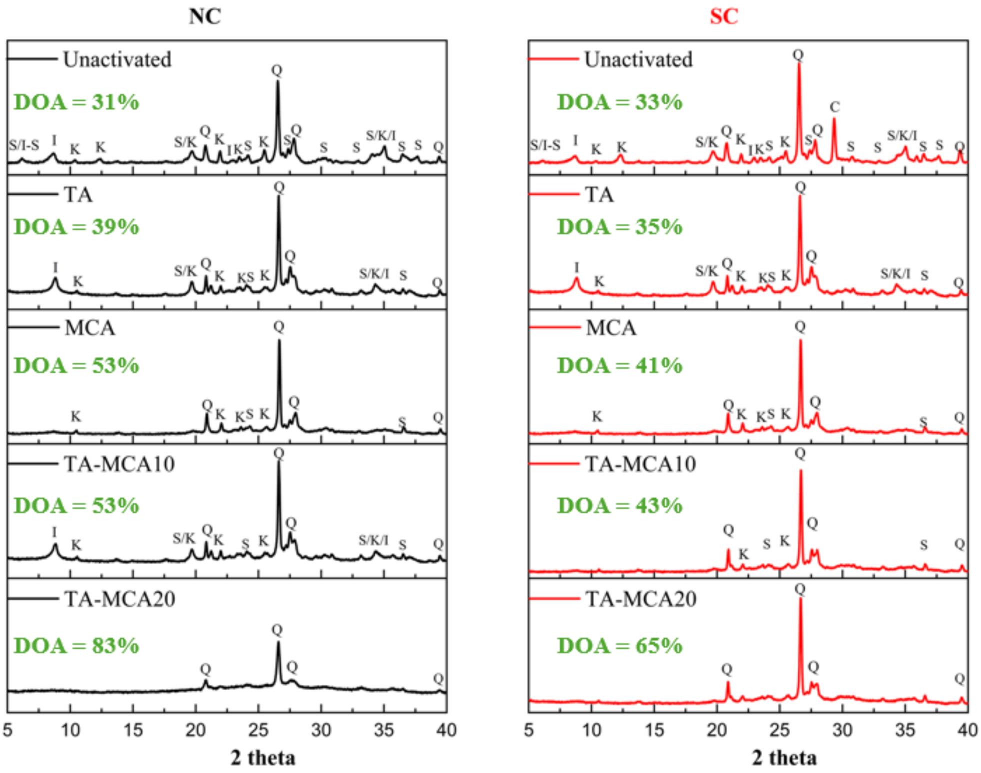
The MR3 protocol consisted of 1 g SCM and 3 g $Ca(OH)_2$ mixed with 3.6 g of 0.5 M KOH solution, with heat evolution monitored at 50 ^{0}C for up to 10 days. Cumulative heat release was used as an indicator of intrinsic chemical reactivity [127].

2.4 KEY RESULTS FROM ACTIVATIONS

The following presents the key compiled findings from the investigations presented in Papers A, B and C. Readers are referred to the respective papers for full datasets and extended discussion.

2.4.1 *Effect of Activations on Mineralogy and Degree of Amorphousness (DOA)*

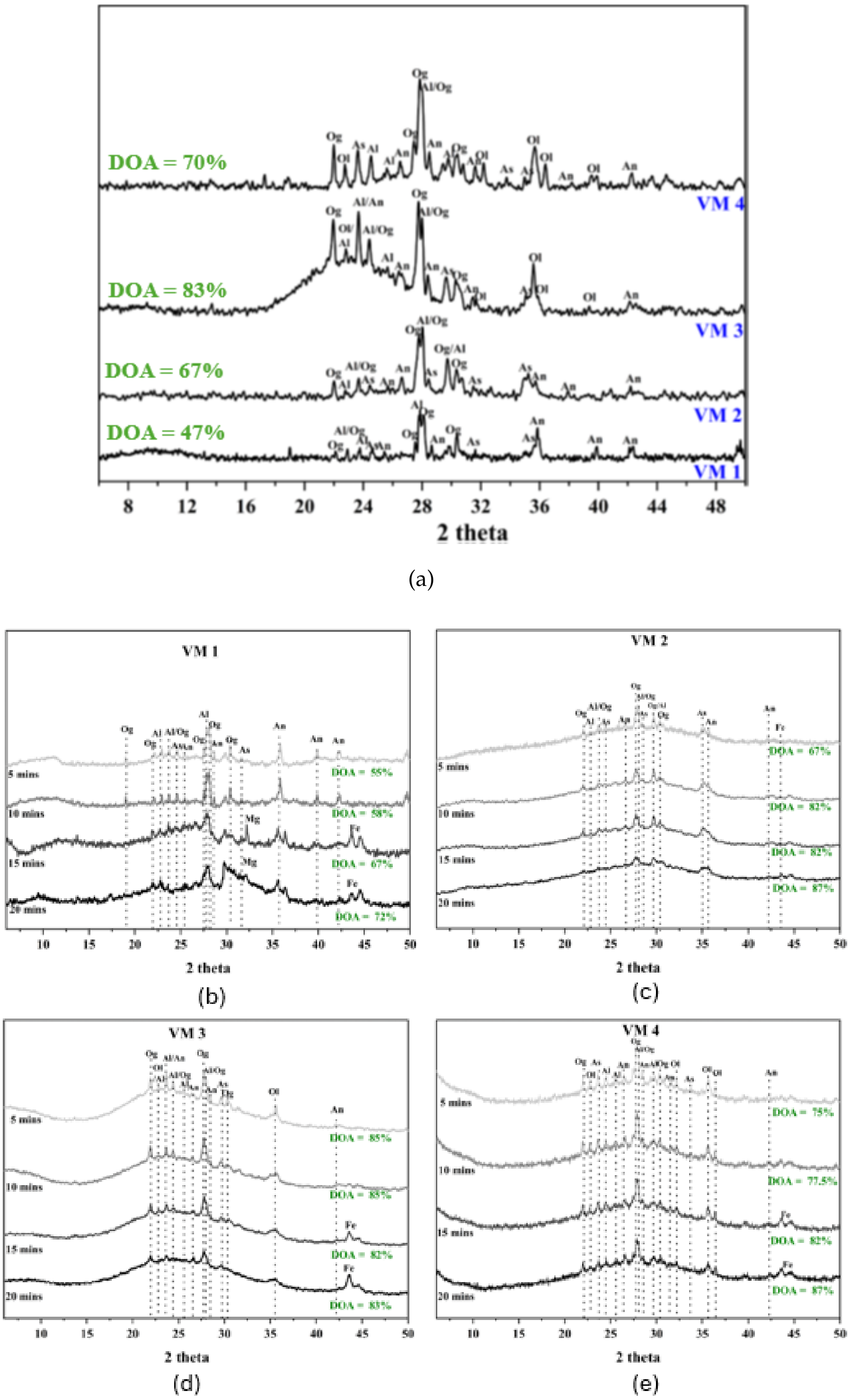
The clays and volcanic materials (VMs) cannot be treated as one SCM category because their starting mineralogies are fundamentally different. As such, the amorphization pathways in both groups of pozzolans are distinct. The clays are multi-phase phyllosilicate systems (NC: 82 % clay minerals; SC: 58 %) containing 18-28 % smectite, 23-33 % illite and 17-21 % kaolinite with possible interstratified illite-smectite, together with non-clay phases (e.g., quartz; calcite in SC). The VMs, in contrast, are dominated by feldspar-group minerals (Albite, Anorthite, Andesine, Oligoclase; plus Olivine in some cases) and exhibit high initial amorphous contents that are further modified by mechanochemical activation. This supports the broader view that activation routes and performance indicators must be mineralogy-specific rather than universal for *natural pozzolans*.



(a) (b)

Figure 3: The mineral phases and amorphous contents of the NC (a) and SC (b). S=smectite, I=illite, K=kaolinite, I-S=illite-smectite, C= calcite, and Q= quartz. (*Adapted from Paper A*)

Figures 3 and 4 shows how activation modifies crystalline phases and amorphous contents in the clays and VMs, respectively. In clays (Figure3 (a)), peak intensities decrease for both clay and non-clay phases, with stronger reductions observed for MCA and strongest through TA-MCA20, indicating more extensive disruption of the phyllosilicate structure than TA alone. These peak reductions reflect progressive loss of crystallinity and increasing amorphization, consistent with previous studies [147, 148]. It is known that MCA can promote disordering and dehydroxylations in illites and smectites that are difficult by TA. In current clays, MCA was not seen to fully amorphize these minerals while maximum amorphization, peak broadenings were only brought about through the combined activations. Quantitatively, TA-MCA20 increased amorphous content in NC by 124 % vs TA and 84 % vs MCA, and in SC by 54 % vs TA and 35 % vs MCA. The lower amorphous levels in SC are consistent with its lower clay mineral fraction (approximately 30 % less than NC), reducing the amount of activatable phyllosilicates.



(a)

(b)

(c)

(d)

(e)

Figure 4: The mineral phases and amorphous contents of the untreated VMs (a), and VMs activated under 4 different treatments (b-e). An= Anorthite, Cr= Cristobalite, Og= Oligoclase, As=Andesine. (*From Paper C*)

A similar overall trend occurs in the VMs (Figure 4 (b)) where increasing MCA duration reduces peak intensities and generally increases amorphous content. However, unlike clays, some VMs show new crystalline phase formation at longer milling (typically ⩾15 min); periclase was consistently detected in VM 1, VM 3, and VM 4. In VM 3, periclase emergence coincided with a decrease in amorphous content at grinding time of 15 min compared to 10 min, whereas in the other VMs new-phase appearance occurred alongside reductions in existing crystalline peaks and an overall continued increase in amorphous content with prolonged MCA.

2.4.2 *Effect of Activation on PSD and SSA*

Activation induces simultaneous changes in PSD and SSA, generally decreasing mean particle size (D50) and increasing SSA in both clays and VMs. However, SSA increases are often disproportionately larger than the corresponding D50 changes, indicating that surface generation through fracture roughening and pore formation contributes beyond simple particle-size reduction. Figure 5 shows the relationship between D50 and SSA for clays (NC, SC) and VMs 1-4 under different activation conditions (four sample points for each). Although in general the surface areas increase as particle size decrease, the relatively low R^2 shows that particle size explains only 23 % of the BET variation. This suggests that, although fineness contributes to surface development, additional factors such as fracture morphology, pore generation, and mineralogical characteristics play a significant role in governing BET. The morphology changes have been presented and discussed in detail in Papers A and C.

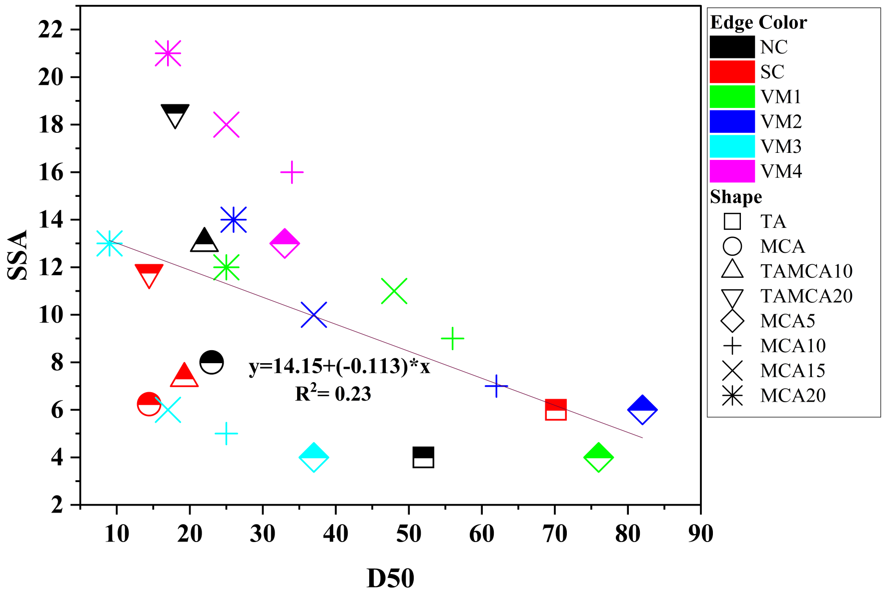


Figure 5: Relationship between D50 and SSA for NC, SC and VMs 1-4 under different activation conditions. The solid line represents the linear regression fit.

For the clays, the strongest modification occurs under combined activation (TA-MCA20). Thermal pre-treatment likely reduces agglomeration and enhances subsequent fragmentation during milling [55], leading to the largest SSA increases. In NC, TA-MCA20 increased SSA by 374% relative to TA and 158% relative to MCA; in SC, the increases were 95% and 87%, respectively. The comparatively lower surface areas in SC are consistent with its calcite-bearing mineralogy, as Ca-related surface deposition can reduce measurable SSA values [149].

For the VMs, increasing MCA duration progressively increased SSA across all materials, even when D_{50} shifts were modest. VM4 showed limited PSD sensitivity but substantial BET-SSA growth, indicating that milling enhances surface area via morphology changes and mesopore creation rather than particle refinement alone [150]. VM4 consistently achieved the highest BET values, suggesting higher intrinsic grindability, which is known to vary in hyaloclastites depending on depositional history [151].

Overall, these results demonstrate that surface development depends not only on fineness but also on activation pathway and mineralogy. In clays, thermal preconditioning enhances fragmentation efficiency, while in glass-rich VMs, microstructural surface generation during MCA plays a dominant role. These findings support the need to interpret activation using coupled physical and structural parameters rather than PSD alone [21].

2.4.3 *Atomic-Scale Al–Si Network Disruption of Clay under TA–MCA*

To further elucidate how activation modifies the local Al–Si coordination environments of the clays, $^{27}Al/^{29}Si$ MAS NMR spectroscopy together with FTIR was employed on NC as a representative low-kaolinite heterogeneous clay. TA, MCA and TA-MCA with 20 mins grinding duration were studied. Paper B shows that the activation routes do not induce the same type of disorder. Instead, they define three distinct atomic-scale pathways: thermal activation (TA) is primarily reorganisation-dominated, mechanochemical activation (MCA) is fragmentation-dominated, and combined TA–MCA leads to extensive network disruption. A schematic of the atomic structure modeled from NMR analyses is presented in Figure 6. Across the spectroscopic disorder descriptors explained in detail in Paper B, the structural disorder increases systematically from the unactivated state to TA, MCA, and finally TA–MCA, demonstrating that the combined treatment induces substantially greater atomic-scale disruption of the aluminosilicate framework than can be explained by particle refinement or amorphousness alone.

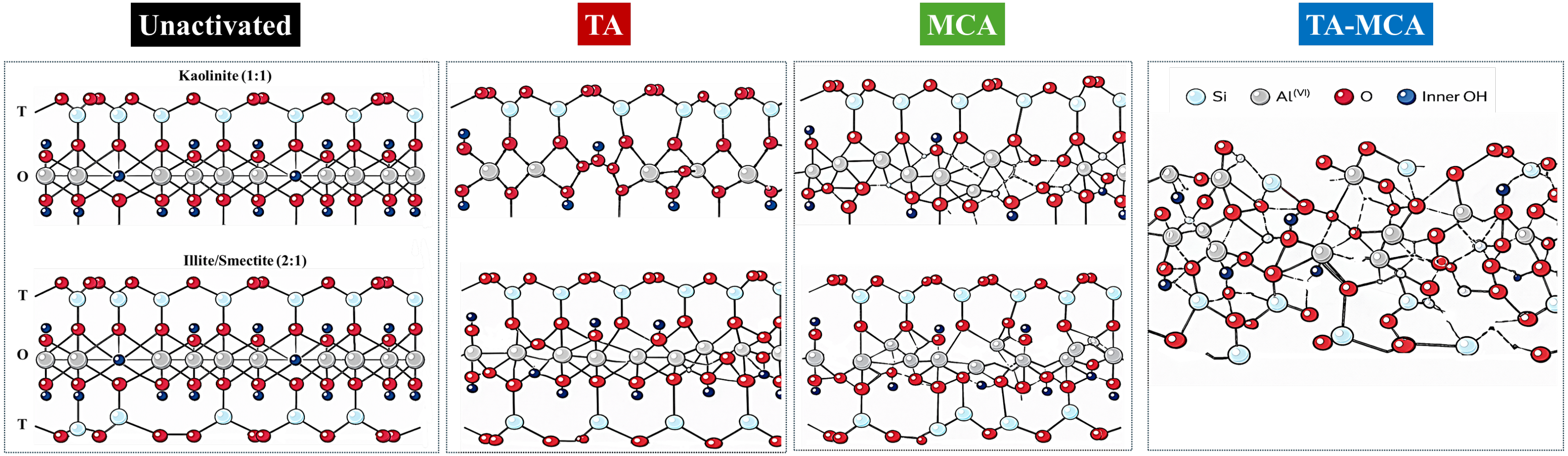


Figure 6: Schematic model of structural changes in 1:1 and 2:1 clay minerals within the natural clay during activation. TA promotes dehydroxylation and Al coordination changes, MCA induces fragmentation and distortion with partial retention of Al(VI), and TA–MCA results in extensive framework collapse and highly disordered aluminosilicate structures, as evidenced by ^{27}Al and ^{29}Si MAS NMR. (*From Paper B.*)

Figure 7 shows the distribution of Al coordination environments after each treatment. In the unactivated clay, the spectrum is dominated by octahedral Al(VI), with deconvolution giving 44.18% Al(VI), 48.88% Al(IV), and only 6.94% distorted Al(VI). After TA, Al(VI) drops sharply to 4.31% while Al(IV) rises to 79.02%, indicating that TA mainly promotes dehydroxylation-driven reorganisation of the octahedral sheet into comparatively ordered tetrahedral environments. MCA follows a different route: Al(VI) is reduced only to 8.25%, while distorted Al(VI) increases to 21.09%, showing that milling primarily broadens the distribution of strained and heterogeneous local environments rather than simply converting octahedral Al into tetrahedral Al. The combined TA–MCA treatment produces the strongest disruption, reducing residual Al(VI) to only 0.50% and increasing distorted Al(VI) to 30.52%, the highest among all samples. Spectrally, the Al(VI) resonance becomes highly broadened and nearly featureless, while the Al(IV) resonance also loses definition, indicating the widest distribution of metastable Al environments. No distinct Al(V) resonance was resolved, suggesting that in this heterogeneous clay the transformation proceeds through a continuum of distorted environments rather than through a stable intermediate Al(V) state.

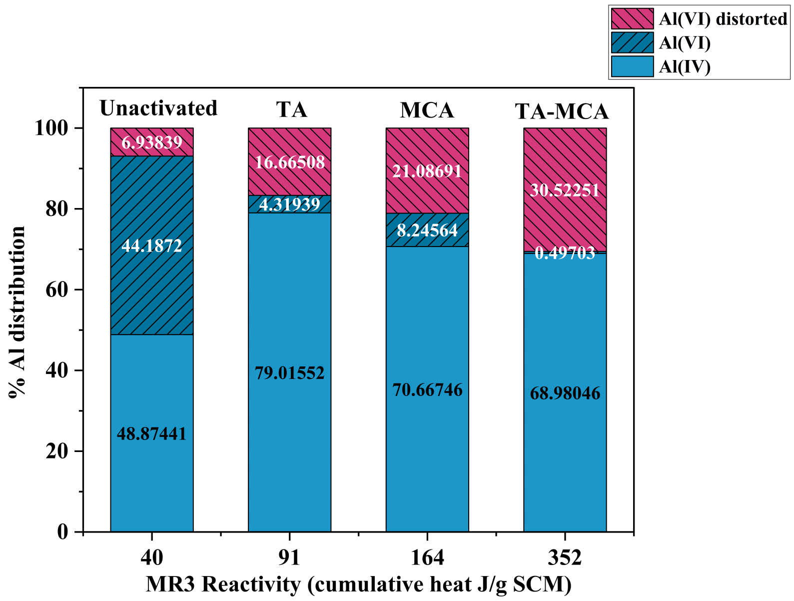


Figure 7: Normalized fractions of Al(VI), Al(V), Al(IV), and distorted Al(VI) in NC clay under different activation treatments derived from ^{27}Al MAS NMR. (*From Paper B*)

The ^{29}Si MAS NMR results complement the findings by showing that activation changes not only Al coordination but also silicate connectivity. The unactivated clay contains a combined Si–Al fraction of about 45% from Q^4(2–3Al) and Q^3(1–2Al) environments. After TA, this rises strongly to about 85%, showing that thermal treatment mainly reorganises the framework and increases Si–O–Al connectivity. In contrast, MCA lowers the Si–Al fraction slightly to about 42%, reflecting cleavage of Si–O–Al linkages and mechanochemical depolymerisation. TA–MCA yields an intermediate Si–Al fraction of about 53%, but with broadened and less well-defined resonances, indicating that the initial thermal reorganisation is followed by mechanochemical breakdown into a decoupled and disordered aluminosilicate network. Thus, TA increases connectivity with moderate disorder, MCA decreases connectivity while increasing disorder, and TA–MCA combines both effects to generate moderate residual Si–Al connectivity together with maximal Al disorder.

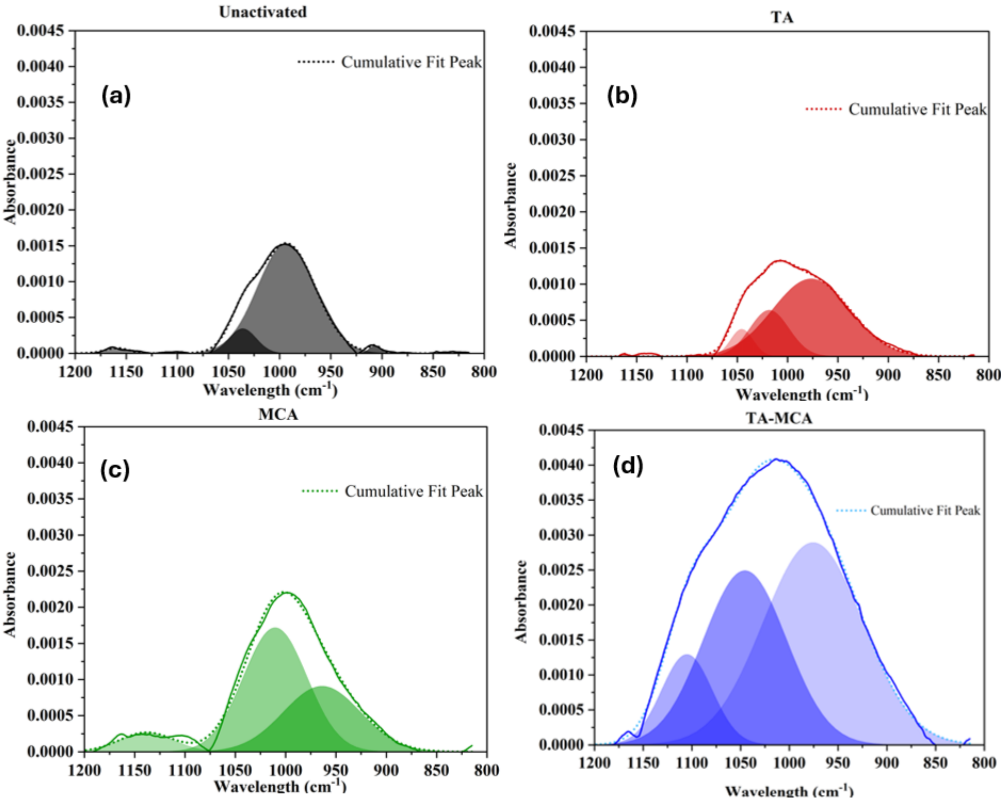


Figure 8: (a-d): Gaussian deconvolution of the Si–O–T stretching region for the clay under different activation states.

FTIR corroborates these NMR observations. The Si–O–T stretching region (1200–900 cm^{-1}) broadens progressively after activation, most strongly for TA–MCA and then MCA, whereas TA shows only a moderate response. Deconvolution of this region is presented in Figure 8, which further clarifies the nature of these changes as follows: the unactivated clay is characterised by a relatively narrow and near-symmetric envelope dominated by a main band around 993 cm^{-1}, while TA produces moderate redistribution into bands near 977 and 1018 cm^{-1}, consistent with a reorganisation-dominated pathway. MCA generates a broader envelope with multiple contributions near 964, 1010, and 1138 cm^{-1}, indicating a more diversified distribution of Si–O–T environments arising from bond distortion, partial depolymerisation, and local rearrangement [152, 153]. TA–MCA produces the broadest and least resolved envelope, dominated by a very broad band around 1005 cm^{-1} together with a broad higher-wavenumber contribution near 1095 cm^{-1}, confirming that the combined treatment yields the widest dispersion of Si–O–T environments and thus the highest degree of silicate-network disorder.

2.4.4 *Correlations of physico-chemical and structural changes to MR3 reactivity*

It was observed that MR3 reactivity rises with activation intensity. For clays, MR3 ranking follows the severity of treatment: TA-MCA20 > TA-MCA10 MCA > TA, with the clearest jump for NC under combined activation (Details presented in Paper A). For VMs, MR3 reactivity increased systematically with milling duration where all VMs reached moderate reactivity after 15 min MCA, and 20 min further increased MR3, with VM4 reaching high reactivity (Paper C). At the same time the governing parameter of reactivity is not universal and MR3 results reflect the combined modifications observed in: (i) amorphous degrees (DOA), (ii) mean particle sizes (D50),(iii) Specific surface areas, and (iv) structure of Al-Si network coordinations.

Synthesizing the results shown in Figure 3, Figure 9 presents the relationship between degree of amorphousness (DOA) and MR3 reactivity for NC, SC, and VMs 1–4, each subjected to four different activation conditions (four data points per material). The plot is divided into quadrants to distinguish low and high DOA–MR3 regions.

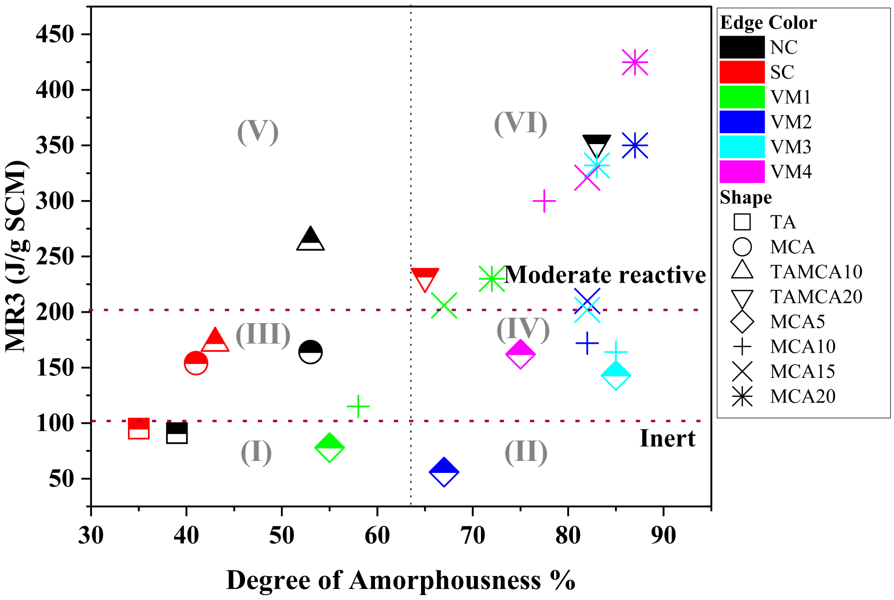


Figure 9: Relationship between degree of amorphousness (DOA) and MR3 reactivity for activated clays (NC, SC) and volcanic materials (VM1-VM4). The dashed horizontal lines depict the reactivity thresholds adopted from [57] and vertical lines divide the plot into quadrants corresponding to low and high DOA and MR3 domains.

Most materials exceeding the moderate reactivity threshold are located at DOA values above approximately 64 % (Quadrant VI). However, several samples with similarly high DOA exhibit only low reactivity (Quadrant IV), and one even falls within the inert region (Quadrant II). Conversely, while most materials below 64 % DOA are classified as inert or low reactive (Quadrants I and III), one sample achieved moderate reactivity despite its lower amorphous content. These observations indicate that although DOA influences reactivity, it alone does not fully govern performance, and additional physical parameters contribute to the overall reactivity response.

Additionally, chemical compositions including amounts of SiO_2, Al_2O_3, CaO and ionic dissolution rates would deeply influence reactivity rates. Bubble plot in Figure 10 shows the combined effect of physical parameters D50, SSA on the MR3 reactivity. Although it was formerly observed in Figure 5 that the relationship between D50 and SSA is only moderately linear, they do collectively impact the reactivity. Figure 10 shows a general clustering trend where high MR3 values (largest bubbles) occur predominantly in the low D50–high BET region (left–upper quadrant). This indicates that materials achieving both particle refinement and substantial surface areas tend to exhibit the strongest reactivity. VM4 consistently occupies this region, suggesting its superior surface development efficiency during activation.

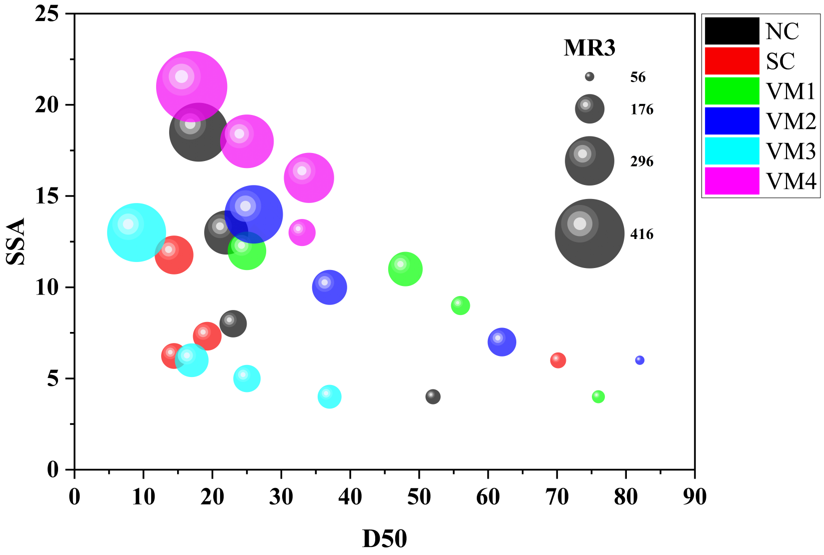


Figure 10: Bubble plot showing the relationship between D50, SSA their collective effect on MR3 for NC, SC and VMs 1-4 under different activation conditions. Bubble diameter sizes represents MR3 reactivity order (J/g SCM).

However, the relationship is not purely linear. Several materials with similar D50 values display markedly different BET and MR3 values. For example, around D50 20–30 µm, BET varies significantly (5–18 m^2/g), and MR3 correspondingly ranges from moderate to high. This indicates that SSA varies between samples even at comparable fineness and this is brought about by

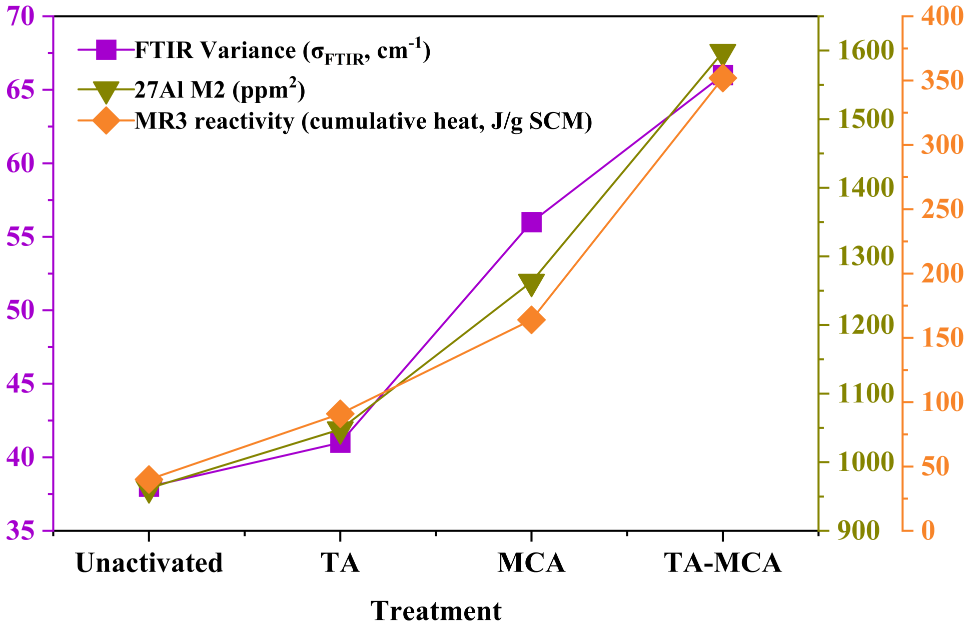


Figure 11: Correlation between M_2 of ^{27}Al MAS NMR, FTIR variance and MR3 reactivity. (*From Paper B*)

morphology. At higher D50 values ($> 50\ \mu$m), BET is generally lower and MR3 is reduced, confirming that coarse materials tend to remain less reactive. Nevertheless, some VMs still show moderate MR3 despite modest BET, indicating the contribution of intrinsic amorphous structure or glass chemistry to reactivity. Overall, Figures 9 and 10 demonstrate that all three aspects of particle size, SSA and material specific amorphousness have been impacted through the activations in varied levels and they combinedly govern the improvements brought about in the reactivity levels.

For studying the effect of activation on clay structures through NMR and FTIR, spectroscopic disorder descriptors were defined in Paper B, to quantify the link between atomic-scale structural changes and measured reactivity. For NMRs, the second moment M_2 takes into account the integrated area of each fitted peak, center positions and peak widths. For FTIR, the variance quantified the area of fitted peak, center wavenumber and width to quantify the spread of vibrational environments within the aluminosilicate network. The correlations between these disorder descriptors and MR3 reactivity are shown in Figure 11.

The second moment (M_2) of the deconvoluted ^{27}Al MAS NMR spectra increased systematically from the unactivated clay to TA, MCA, and TA–MCA, and correlated strongly with MR3 reactivity ($R^2 = 0.96$). This indicates that reactivity is governed not simply by the relative fractions of Al(IV) and Al(VI), but by the overall spread of dissolution-prone Al environments generated during activation. In contrast, the second moment of the ^{29}Si MAS NMR spectra did not show a similarly direct linear correlation with MR3 reactivity, since it primarily reflects the mode of silicate-network evolution, i.e., reorganisation, fragmentation, or network disruption, rather than the extent of chemically reactive disorder itself. Similarly, the FTIR variance descriptor σ^2_{FTIR} increased progressively from the unactivated clay to TA, MCA, and TA–MCA and also correlated strongly with MR3 reactivity ($R^2 = 0.94$). Taken together, these results show that TA–MCA generates the broadest distribution of metastable aluminosilicate environments and that the enhanced reactivity of the clay is governed by atomic-scale structural disorder of the Al–Si network rather than by physical refinement alone.

2.5 SYNTHESIS AND IMPLICATIONS FOR HYDRATION

Taken together, the findings in this chapter show that activation cannot be interpreted through a single governing variable, nor transferred directly between different natural pozzolan families without mineralogical context. In the low-kaolinite clays, the most effective route was the combined thermo-mechanochemical treatment, which produced the greatest disruption of phyllosilicate structure, the strongest modification of Al-Si coordination environments, and the highest resulting reactivity. In the volcanic materials, MCA alone was sufficient to produce substantial changes in amorphous content, surface development, and reactivity, although the response remained material-specific and dependent on the original mineralogical and chemical composition.

A second key outcome is that measured reactivity reflects the combined effects of structural disorder, physical refinement, and precursor chemistry, rather than any single descriptor such as degree of amorphization, particle size, or surface area considered in isolation. The activation stage therefore serves not only to improve reactivity, but also to define the chemical state in which reactive Al and Si species become available for subsequent hydration. In this way, Chapter 2 provides the basis for the rest of the thesis. Among the tested mechanisms and sample sets, the study shows which activation routes were effective to produce SCMs that are reactive enough to be studied further in blended cement systems.

This also provides the transition to Chapter 3. Once activation has altered the original structure and reactivity, the next question is no longer whether the material reacts, but how it reacts within Portland cement blends, how the released species are partitioned into hydrate phases, and how those pathways influence strength development and pore structure evolution. The hydration investigations that follow therefore build on the activation-reactivity relationships established here, with particular attention to the fate of reactive aluminum in clay- and VM-based systems. For the volcanic materials, this link is conceptual rather than material specific, since Chapter 3 examines hydration in an industrially available Mg-rich VM selected for binder relevance, rather than in one of the four VMs screened here for activation response.

3

HYDRATION AND ELEMENTAL PATHWAYS OF ALUMINUM

This chapter presents the mix design of blended systems incorporating activated clays and volcanic materials, and examines hydration evolution and the pathways of aluminum during hydration. It builds on the activation framework established in Chapter 2. In particular, the chapter shifts the focus from how activation changes the starting SCM state to how those activated materials hydrate and influence binder development in Portland cement systems. It synthesises the findings from Papers D and E with focus on binder design, phase development, and microstructural evolutions. Detailed material descriptions, experimental procedures, complete datasets, and full analyses are therefore not repeated in detail here, but are instead presented in the appended papers, which constitute the primary scientific contributions of this work.

3.1 HYDRATION CHEMISTRY IN POZZOLANIC BINDER SYSTEMS

3.1.1 *Context on Clay Binder Hydrations*

Archaeological evidence shows that clay-rich earths were used extensively as binder for bricks, mortars, and plasters in Mesopotamia, the Indus Valley, ancient China, and the Mediterranean, long before the emergence of hydraulic binders [87, 154, 155]. In these early applications, material performance was governed primarily by particle packing, plasticity, and consolidation through drying or low-temperature firing, rather than by hydration-driven chemical binding. Nevertheless, these practices established an empirical understanding that finely divided aluminosilicate materials could be engineered to produce durable construction elements when appropriately processed. Although the atomic-scale mechanisms were not understood at the time, these systems exploited the dissolution of reactive aluminosilicates and their interaction with calcium to form binding hydrates, laying the conceptual foundation for the modern definition of pozzolanic reactivity.

In the context of contemporary decarbonisation efforts clay re-emerged as an intentional SCM, driven by the need to reduce clinker content while maintaining performance [17, 42]. Within this renewed focus, kaolinite-rich calcined clays have received disproportionate attention as presented in Chapter 1. However, that has laid the ground work for understanding and building up knowlege on other clay systems. Upon calcination, kaolinite transforms into metakaolin, a highly disordered aluminosilicate with rapid dissolution kinetics under alkaline conditions. In hydrated cement systems, silicon and aluminum released from metakaolin readily incorporates to form C-(A)-S-H and remaining Al participates in the formation of AFm phases, particularly space-filling carboaluminates in the presence of limestone. This synergy enables high clinker replacement levels with sufficient strength and enhanced pore structure enhancement [42, 61].

Contrastingly, clays dominated by 2:1 mineralogy generally contain lower reactive aluminosilicate contents and have consistently demonstrated comparatively low pozzolanic reactivity, limited limestone synergy, and less favourable hydration kinetics when used as SCMs [74, 81, 156–158]. This behaviour has traditionally been attributed to intrinsic mineralogical constraints, as illite and smectite rich structures possess more stable phyllosilicate layers that resist dehydroxylation and structural disruption. However, the findings in Chapter 2 demonstrate that reactivity is directly controlled by the degree of disruption of the Al–Si coordination network, beyond bulk dehydroxylation and particle-size effects. In mixed-mineralogy clays, even MCA may fail to induce extensive structural distortions of Al-Si coordinations or achieve complete dehydroxylation, particularly when multiple clay and non-clay phases coexist. If the Al–Si framework remains only partially unlocked, dissolution becomes kinetically constrained which would limit the release of reactive Al and Si species [40, 81, 159], and thereby restricting the necessary hydrate formation. Therefore, for clays with chemistries fundamentally distinct from kaolinite-rich systems, this necessitates an alternative activation strategy, as was presented in preceeding chapter. The combined thermo-mechanochemical (TA–MCA) route was shown to induce the highest degree of structural disorder and amorphization, along with highest surface area and particle size modifications, all of which potentially maximized reactive species availability. Such atomic-scale disruption directly would be governing subsequent hydration behaviour and cannot be inferred from fineness or bulk reactivity metrics alone. Under these conditions, hydration evolution in combined activated low-kaolinite clay systems becomes governed not by the presence of clay type, but by how the disrupted reactive species like aluminum contributes to hydrate phase development.

In this light, the present study investigates blended systems incorporating the combined activated heterogeneous clay (NC) described in Chapter 2 to understand their hydration evolution in blended form. Binary clay–OPC systems were examined alongside binary limestone–OPC mixes to distinguish true pozzolanic contributions from physical filler effects. Ternary clay–OPC–limestone systems were additionally evaluated to assess whether synergistic interactions between released alumina and carbonate species could enable higher OPC substitution levels compared to binary formulations. This addresses research question 3 in the context of clays.

Central to this investigation is aluminum availability and partitioning during hydration. Unlike LC3-type binders, where abundant reactive alumina promotes extensive carboaluminate formation, activated low-kaolinite clays provide a comparatively reduced and potentially kinetically delayed Al supply. This raises key questions regarding whether dissolved aluminum preferentially incorporates into C-(A)-S-H or participates in AFm/carboaluminate formation. Clarifying this competition is essential to understanding phase assemblage development and determining whether limestone contributes chemically through carboaluminate stabilization or functions primarily as a filler in these systems. This addresses RQ 4 in the context of clays.

3.1.2 *Hydration Evolution in VMs*

Unlike clays, VMs do not constitute a single, mineralogically or chemically coherent SCM class. Their composition is even more diverse and governed by magma chemistry, cooling environment, and post-depositional alteration history, resulting in wide variability in glass content, Al availability, and the presence of Mg-, Fe-, and Ca-bearing phases [46, 47, 54, 117]. As a result, hydration behaviour across volcanic SCMs exhibits a great scatter.

Much of the existing literature on volcanic SCMs has therefore focused on macroscopic performance indicators, such as compressive strength development, hydration kinetics, or durability-related properties, often for individual volcanic sources [46, 47, 160]. While existing studies have demonstrated that meaningful clinker replacement is achievable, they have provided limited mechanistic insight into hydrate phase development. Often, the findings are less transferrable among varying groups and become deposit specific. Additionally, volcanic materials are frequently interpreted through analogies to either fly ash or latent hydraulic slags, despite having bulk chemistries that differ substantially from both classes.

As established in Chapter 2, volcanic materials can span a broad compositional space, ranging from moderate silica, alumina-lean systems to basaltic compositions enriched in MgO and Fe_2O_3, with moderate CaO contents. This chemical diversity sets them apart from either industrial SCMs or natural pozzolans. Under these circumstances, hydration evolution in volcanic systems warrant mechanistic understanding of how the different chemical composition affects or controls phase formations and performance. Specifically in these contexts, how available aluminum is partitioned among C-(A)-S-H, AFm/AFt phases, and, where Mg is present, Mg–Al layered double hydroxides.

In particular, existing studies reveal recurring gaps: (i) MgO is commonly treated only as a bulk oxide, with little insight into its incorporation into specific hydrate phases; (ii) hydrate characterization relies mainly on XRD and TGA, which are insensitive to poorly crystalline Mg-bearing phases; (iii) hydrotalcite-like Mg-Al layered double hydroxides are often inferred indirectly; and (iv) aluminum availability is interpreted using fly ash or slag analogies, overlooking Mg-driven competition that redistributes Al away from C-(A)-S-H and carbonate-AFm phases. As a result, the role of MgO in strength development, pore refinement, and limestone synergy remains unclear.

A clear understanding of how these oxides behave during hydration is necessary to predict the performance of VMs. While case-specific bulk performance results provide useful benchmarks [47, 49, 122, 161], they do not fully explain the underlying reaction processes. It is important to understand how reactive oxides interact and contribute to hydrate formation which is necessary to develop mix design approaches that are both reliable and transferable across different volcanic SCMs.

This chapter presents the results of hydration investigations performed on a basaltic VM. Similar to clays, both binary and ternary substitutions are studied to assess bulk binder performances such as compressive strength, pore structure and hydrate phase evolution. Additionally, distribution of Al in associated hydrate phases are studied. Taken together, they address research questions 3, 4 and 5 in the context of VMs.

3.1.3 *Aluminum Partitioning as a Basis for Comparison*

Across both material families, aluminum is treated in this chapter as the main mechanistic variable because it connects the reactivity of the activated materials to hydrate formation, limestone interaction, and microstructural development. In the clay systems, the main question is whether the available reactive alumina enters C-(A)-S-H or also forms AFm/carboaluminate phases, since this affects whether limestone acts mainly chemically or mainly as a filler [162, 163]. In the volcanic systems, as presented earlier, the prior expectation is not well defined as the question becomes more complex because aluminum may be distributed among C-(A)-S-H, AFt/AFm phases, strätlingite, in Fe-bearing systems siliceous hydrogarnet, and in Mg-bearing systems hydrotalcite -like layered double hydroxides which are additional sinks for the aluminum [62, 164–168]. For this reason, aluminum partitioning provides the clearest common basis for comparing how these different SCM systems hydrate and develop performance.

3.1.4 *Effect of Varying Limestone Particle Size on Binder Synergy*

In addition to the main binder comparisons, a targeted supplementary assessment was also conducted to examine the effect of varying limestone particle sizes on the reactivity of the binders in both the clay and volcanic systems. This provides an additional perspective on whether increased limestone fineness can enhance limestone synergy through filler, nucleation, or carbonate-related effects, and is included here as a complementary extension to the main studies.

3.2 BINDERS, MIX DESIGN AND EXPERIMENT METHODS

3.2.1 *Binders*

The clay used in the hydration study is thermo-mechanochemically activated clay, earlier presented as NC in Chapter 2. This clay was chosen due to its superior response to activation. The activated natural clay is hereafter referred to as CC.

The VM used in the hydration study is from Lambafell, in southern Iceland, and is distinct from the four volcanic materials screened in Chapter 2. While Chapter 2 examined mechanochemical activation across several mineralogically different Icelandic VMs, the purpose of Chapter 3 is to investigate blend design, hydration pathways, and aluminum partitioning in a representative Mg-bearing volcanic binder system. The material used here is a southern Icelandic hyaloclastite, classified as a basaltic hyaloclastite formed through explosive volcanic fragmentation under subglacial or subaqueous conditions [169]. It is compositionally related to the southern Icelandic volcanic materials considered in Chapter 2 and is closest in mineralogy to VM1, although it contains a higher MgO content. The material was already available in an industrially ground state and was therefore selected to provide a more application-relevant basis for the hydration investigations [170]. This also avoided additional laboratory preparation and allowed the hydration study to focus directly on the mechanisms in an already available binder material.

The VM was dried and ground in a cement ball mill by Heidelberg Materials in Dagerhamn, Sweden, to a median particle size of approximately 7 ± 2 μm, corresponding to a specific surface area of about 1.5 m^2/g. This fineness is comparable to the fineness of the high reactive VMs 3 and VM4 that were obtained after 20 min of MCA in Chapter 2. Based on MR3 calorimetry [56], the VM was classified as a medium-reactivity pozzolan [57], with a cumulative heat of 300 ± 25 J/g SCM after 10 days of isothermal calorimetry.

Ordinary Portland cement (OPC) CEM I 52.5 R, supplied by Heidelberg Materials (Skövde, Sweden), was used as the primary clinker source. Limestone used in the ternary systems was Limus 15, supplied by Nordkalk AB (Ignaberga, Sweden), selected for its well-defined chemical composition and controlled particle size. Two additional limestone grades with differing fineness (KÖ100, C7 and Enrich C) were employed selectively for kinetic assessments related to limestone particle size effects. Table 3 presents the oxide composition of the binders used for the studies on hydration evolution along with their mean particle sizes (D50). Additionally, a polycarboxylate ether (PCE)-based superplasticizer containing a clay-blocking functionality was used in clay-containing mixes to ensure adequate dispersion and workability.

Table 3: Chemical composition (by weight percentage) of the materials

Oxides (wt%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	LOI (±2)	Total	D50 (±1)(μm)
CC	51.80	18.35	9.55	1.32	3.34	1.70	8.15	99.86	16.0
VM	48.10	14.60	12.05	12.15	10.15	1.99	-0.01	101.03	7.15
OPC	19.60	4.50	3.00	63.50	3.50	0.27	2.50	99.53	10.00
Limus 15 (LS)	9.00	0.60	0.30	49.50	-	0.10	-	100	41.6
K100 (LS-M)	9.00	0.60	0.30	49.50	-	0.10	-	100	15.10
C7 (LS-S)	9.00	0.60	0.30	49.50	-	0.10	-	100	7.00
Enrich C (LS-F)	9.00	0.60	0.30	49.50	-	0.10	-	100	0.10

3.2.1.1 *Mix design*

Binder proportions were defined using statistically guided mixture design approaches for both the clay and VM based systems. A Scheffe quartic model was used in the Design-Expert (Stat-Ease) software to design binary and ternary mix proportions using CC, VM, LS that substituted OPC up to 50%. This generated 15 workable mix proportions for each pozzolan type including OPC and the binary LS-OPC mixes, to assess effective binder designs based on their hydration evolution and performances. A description of the Scheffe model and logic selection for the binders is presented in the method section of Paper D. For both CC and VM systems, the binary blends were evaluated against LS binary blends to account for potential filler effects. The ternary binders were assessed to investigate possible aluminate–carbonate synergies.

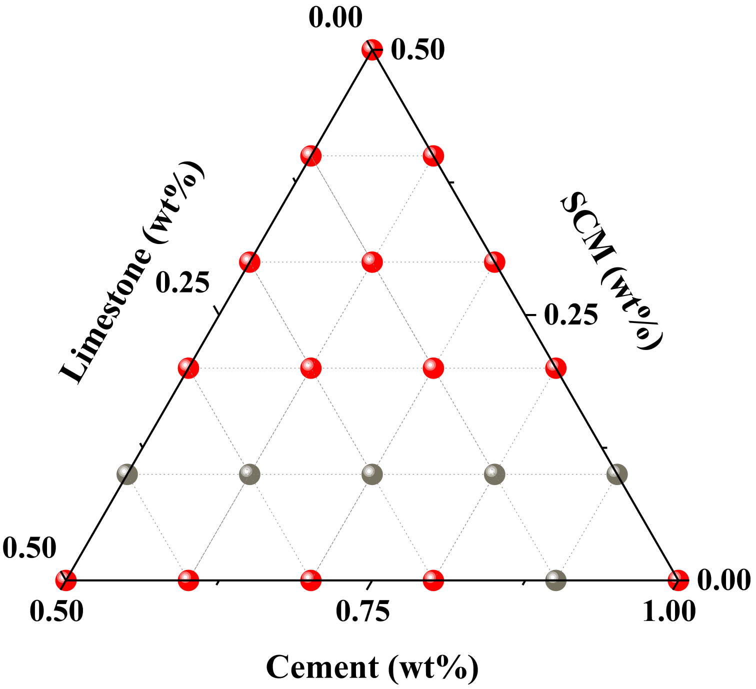


Figure 12: Ternary plot representing the design space for the mix proportions. Red dots represent the proportions that were studied and grey dots represent the statistically suggested mixes that were not considered due to lower replacement potential.

Figure 12 shows the statistically designed mix proportions. 15 mixes, indicated by red dots, were adopted from the model generated mixes. Mixes where the OPC subsitution was below 20 % and majority of mixes where the proportion of limestone was higher than that of SCM, were avoided, as additional limestone is expected to behave as unreacted fillers after the available alumina has been used [171–173]. For each pozzolan type, all 15 mixes were tested for compressive strength, which served as the primary benchmark for selecting representative mixtures for subsequent investigations, including microstructural characterization and hydrate phase evolution. Across both studies, water-to-binder ratios were kept constant at 0.5 to isolate compositional effects on hydration evolution.

Table 4: Mixes used in the study and their corresponding proportions

No.	**Mix name**	**CEM I (OPC) wt %**	**CC or VM wt %**	**Limestone (LS) wt %**
1	OPC	100	0	0
2	CC20	80	20	0
3	CC30	70	30	0
4	CC40	60	40	0
5	CC50	50	50	0
6	CC20LS10	70	20	10
7	CC30LS10	60	30	10
8	CC40LS10	50	40	10
9	CC20LS20	60	20	20
10	CC30LS20	50	30	20
11	CC20LS30	50	20	30
12	LS20	80	0	20
13	LS30	70	0	30
14	LS40	60	0	40
15	LS50	50	0	50
16	VM20	80	20	0
17	VM30	70	30	0
18	VM40	60	40	0
19	VM50	50	50	0
20	VM20LS10	70	20	10
21	VM30LS10	60	30	10
22	VM40LS10	50	40	10
23	VM20LS20	60	20	20
24	VM30LS20	50	30	20
25	VM20LS30	50	20	30

Table 4 presents all the mixes that were investigated and presented in Papers D and E. This chapter presents the strength and pore structure evolutions in blends of both categories of SCM, whereas for more targeted comparisons, seven blends are considered, namely: OPC, CC30, CC30LS10, VM30, VM30LS10, LS 30 and LS40. These representative mixtures were selected because they capture the main mechanistic trends observed across the wider mix matrix that is further detailed in the Papers D and E. Among these, the binary blends represent substitution levels at which the activated SCMs showed clearly measurable hydration and microstructural effects while still maintaining comparable mechanical performance to 100% OPC mix. The selected ternary blends were chosen to examine whether limestone introduced additional benefits beyond those observed in the corresponding binary systems, and therefore provide a clear basis for comparing aluminum partitioning, phase assemblage development, and pore refinement.

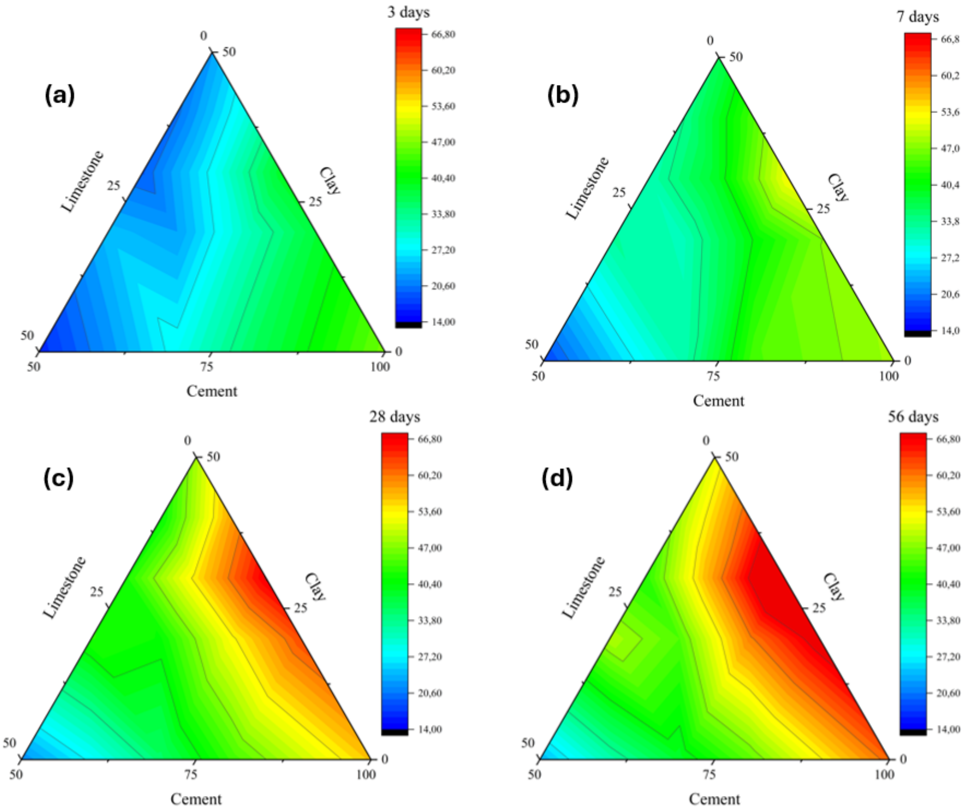
3.2.1.2 *Experimental Methods*

Compressive strength development was measured on mortar specimens at multiple curing ages to capture both early and late hydration behavior, with particular emphasis on later ages relevant for slowly reacting SCM systems. For clays that showed faster strength development, strength was monitored on specimens of 40x40x40 mm at 3, 7, 28 and 56 days. For VMs, mortar prisms of 40x40x160 mm were cast and the strength at 91 days was additionally assessed. Strength testing was conducted in accordance with EN 196-1 [174] using calibrated compression testing machine (Matest 300 kN). Hydrate phase assemblage were assessed on pastes that were cured till 3,7,28 and 56 days. Hydration stoppage for samples was conducted by solvent exchange method with isopropanol that was followed by vacuum drying. Pore structure evolution was assessed on hardened mortar specimens using mercury intrusion porosimetry (MIP) in MicroActive Autopore V 9620. Detailed sample preparation steps are presented in the papers. Phase assemblage evolution was characterised using X-ray diffraction (XRD) in BrukerD8 Discover over 2 theta range of 5-60 °, on powdered paste samples. Thermogravimetric analysis (TGA) in TGA/DSC 3+ Mettler Toledo, and it was used to quantify mass loss associated with bound water and portlandite decomposition. Derivative thermogravimetric curves were used to estimate relative changes in portlandite content and overall hydrate formation between curing ages and binder compositions. ^{27}Al MAS NMR was used to distinguish aluminum present in tetrahedral and octahedral coordination, enabling differentiation between aluminum incorporated into C-(A)-S-H and that present in AFm or other aluminate-bearing hydrates. For clays, ^{29}Si MAS NMR was used to assess silicate chain polymerisation and mean chain length in C-(A)-S-H. Both NMR spectra were obtained using a Bruker 4 mm MAS BB/1H probe at 298 K.

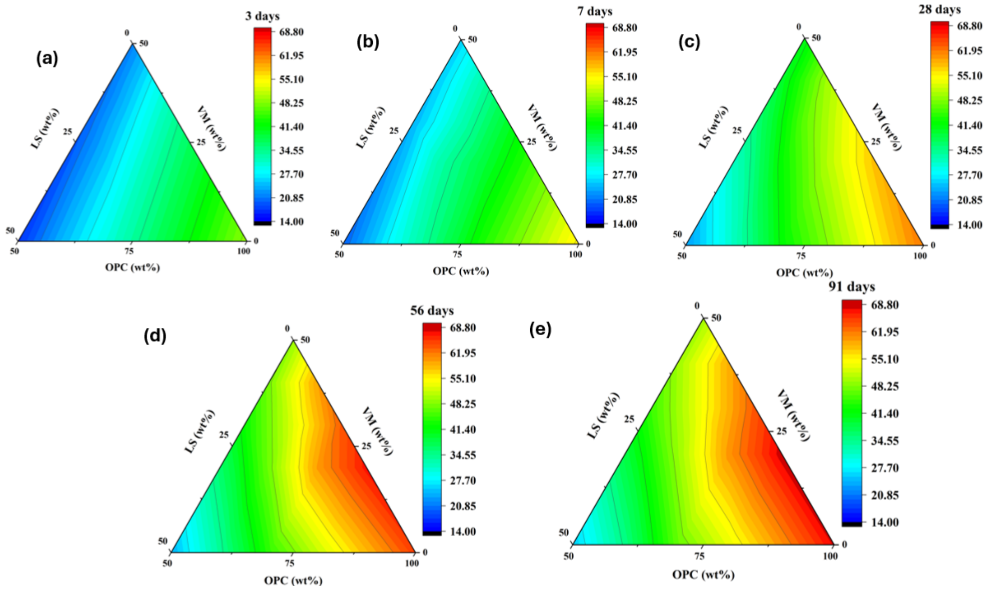
3.3 KEY RESULTS OF EVOLUTION OF HYDRATION

3.3.1 *Correlations between Evolution of Strength, Pore Structure and Phase Assemblage*

The strength evolution for the blends are presented in Figure 13. It illustrates the time-dependent evolution of compressive strength in the SCM-containing systems, where cooler colours indicate lower strength and warmer colours indicate higher strength. The ternary contour plots show that strength development is not static, but progressively increases with curing age from 3 to 56 days.



(a)



(b)

Figure 13: Compressive strength evolution of the matrix over time at 3, 7, 28 and 56 days of clays (a) and VMs including on 91 days (b). The warmer colour shades represent blend proportions of higher strength. (*From Papers D and E.*)

In Figure 13 (a) it can be observed that mixtures containing higher clay contents already begin to exhibit comparatively higher strength levels from 7 days onward, particularly in the range of about 20–30 % clay. This trend becomes more pronounced with time, indicating continued reactivity and microstructural development in the clay-bearing blends. By 56 days, the strength domain shifts markedly towards the clay-rich side, and even binary blends containing up to 40 % clay exceed the strength of OPC. In Figure 13 (b), it can be observed that the VM-containing mixtures are slower in strength development than the clay-containing systems. While early-age strengths remain relatively modest, the contours progressively shift towards warmer colours with curing time, especially from 28 days onward. Mixtures containing about 20–30 % VM begin to exhibit clearer strength benefits at later ages, and this tendency becomes more evident by 56 and 91 days, reflecting continued but slower reactivity and microstructural densification in the VM-bearing blends.

Quantitatively, in the activated low-kaolinite clay systems, binary blends with 30 wt.% OPC (CC30) replacement achieved compressive strengths approximately 10–25 % higher than OPC at 7 and 56 days, despite kaolinite contents below those typically associated with LC3 binders. This strength enhancement was accompanied by a 40 % reduction in total porosity by 56 days, primarily through capillary pore refinement rather than a decrease in total pore volume, and with a high proportion of gel pores at 30–40 % substitution (CC30, CC40). ^{27}Al NMR analysis indicated substantial incorporation of Al(IV) into C-(A)-S-H, which likely contributed to the increased gel pore fraction and associated strength development. Ternary blends containing limestone (CC20LS10, CC30LS10, etc.) did not show systematic strength improvement relative to binary clay blends at similar replacement levels. For binary blends, Portlandite (CH) content decreased over time compared to OPC, confirming ongoing pozzolanic reaction. Hydrate water content (C-(A)-S-H, AFm, AFt, and CH) increased progressively with curing age for all blends.

For the VM systems, clinker replacements of 20–30 % produced compressive strengths comparable to OPC at 56 days, despite lower early-age strength (lower than 7 days) and continued strength gain between 28 and 56 days. Total porosity decreased by 18–22 % over the same period, yielding pore structures similar to OPC at later ages, though with a somewhat higher gel pore fraction in certain compositions. Limestone-containing volcanic blends exhibited consistently lower strengths than their binary counterparts. As observed in the clay systems, CH content declined with curing time, indicating pozzolanic activity, while total hydrate water increased across all VM blends.

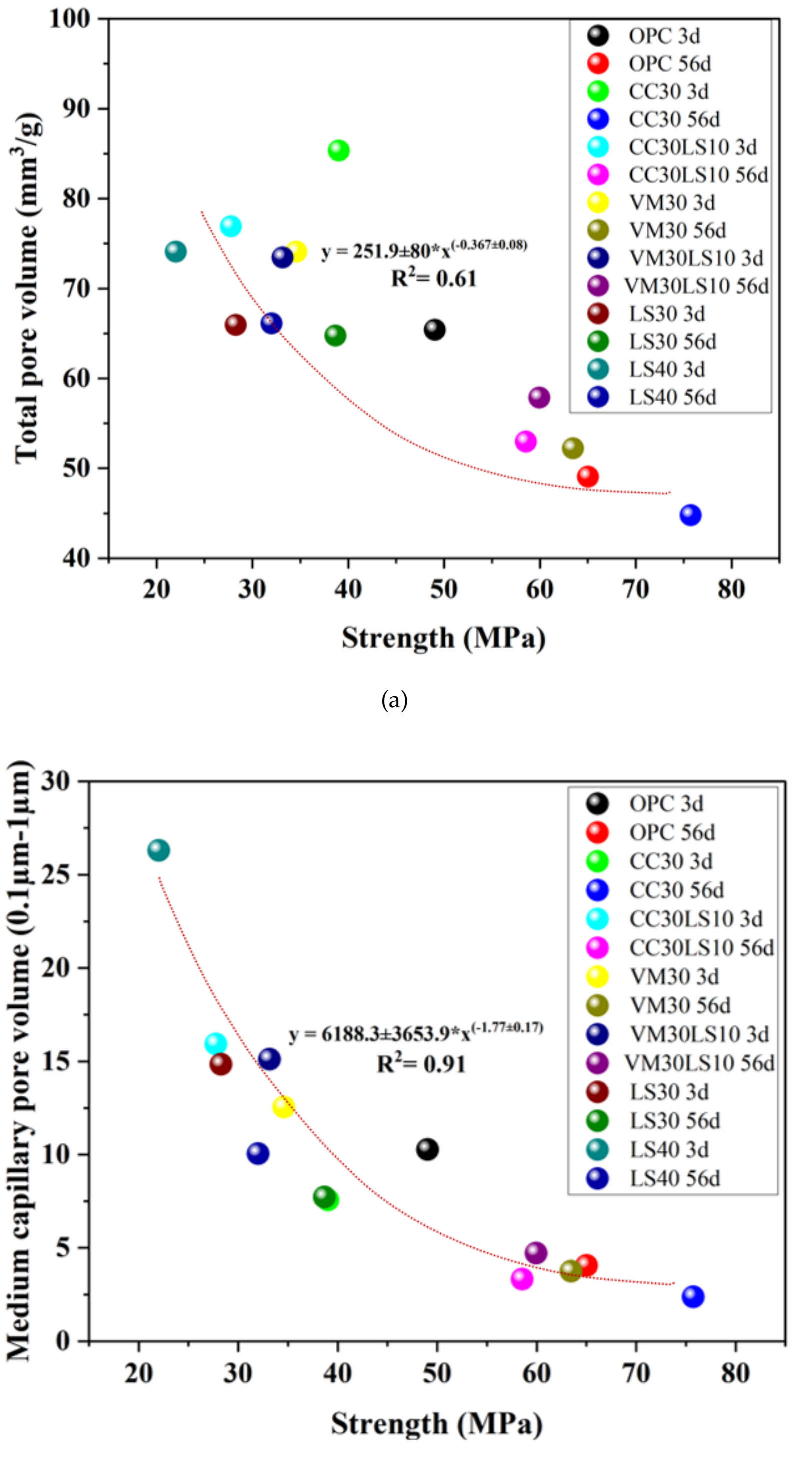
Figure 14 shows the relationship between compressive strength and pore structure for the studied binders. Overall, pore volume decreases and strength increases from 3 to 56 days for most blends, with the clearest improvement observed in the activated clay system, where the 56-day CC blend reaches the highest strength together with the lowest total pore volume among the plotted mixtures. The correlation with total porosity (Figure 14 (a)) is only moderate (R^2 is 0.61), indicating that total pore volume alone does not fully explain the strength development. In contrast, the volume of medium capillary pores in the range 0.1–1 µm shows a much stronger inverse relationship with strength (R^2 of 0.91) (Figure 14(b)). This suggests that the refinement of strength-relevant capillary pores is more decisive than total porosity alone, as further explored in Paper D.

Figure 15 complements this by mapping porosity, hydrate-water content, and compressive strength in a single plot for the representative blended systems at the replacement levels shown. The general trend is that the 56-day mixtures shift towards lower porosity and, in most cases, higher hydrate-water contents than their corresponding 3-day states, which is reflected in the larger bubble sizes. OPC occupies the low-porosity, high-hydrate, high-strength region and therefore serves as a useful reference for microstructural efficiency. The clay- and VM-containing systems lie in an intermediate domain, but they do not evolve identically. At later age, the activated clay blends move more clearly towards the low-porosity / high-strength region, whereas the VM blends generally remain at somewhat higher porosity for comparable strength. This indicates that, even when comparable hydrate-water contents are measured, the hydrates formed in the two systems are likely distributed differently in space and contribute differently to pore refinement. In this sense, the bubble plot suggests that porosity remains the dominant control on strength, while hydrate formation provides an additional positive contribution by progressively filling and refining the pore network.

Among the blended systems, the activated clay binders appear to densify the microstructure more efficiently than the volcanic blends at comparable replacement levels, in line with the broader findings of Papers D and E. The thesis summary indicates that Paper D identified dense microstructures and polymerized C-(A)-S-H in the activated clay binders, whereas Paper E showed that VM systems are additionally influenced by precursor chemistry, especially MgO and Fe_2O_3 which affects aluminum partitioning and the extent of synergy with limestone. Limestone-only substitution remains in the comparatively high-porosity, low-hydrate, and low-strength region, consistent with its more limited chemical contribution and primarily filler-type role. Overall, the figures show that strength development in these binders is governed by the combined effects of pore refinement and hydrate formation, with the clay-based systems achieving the most efficient microstructural densification among the non-OPC blends shown.

3.3.2 *Aluminum Partitioning Mechanisms and its Effect on Microstructure*

A key shared outcome across both studies is that Al partitioning controls hydrate assemblage development. In the low-kaolinite clay systems, solid-state NMR showed that aluminum preferentially incorporated into C-(A)-S-H, rather than forming AFm phases. This preferential uptake increased silicate chain length and produced mechanically robust matrices despite limited carboaluminate formation. As a consequence, limestone addition did not result in the classical LC3-type synergy, as available aluminum was largely consumed by



(b)

Figure 14: Correlation of compressive strength with total pore volume (a) and medium capillary pore volumes (b) in CC and VM blends.

C-(A)-S-H. Figure 16 presents the intensities of Al species corresponding to their incorporations in phases C-(A)-S-H, Strätlingite, AFt and AFm/Ht.

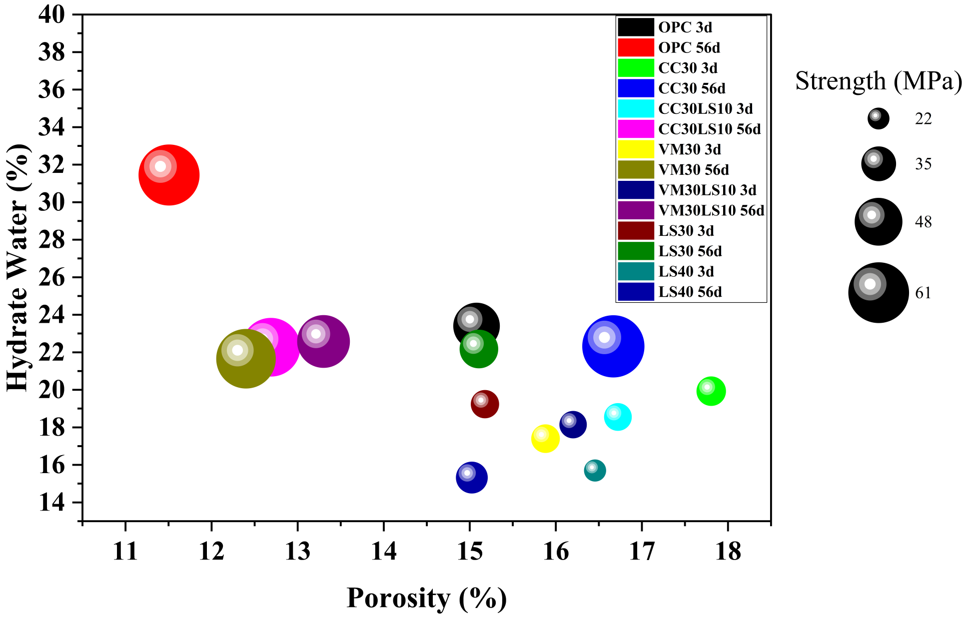


Figure 15: Relationship between total porosity and hydrate water content for OPC and blended systems. Bubble area represents intensity of compressive strength (MPa).

Aluminum is clearly partitioned among multiple hydrate phases in both systems, but the distribution pathways differ. The VM blend contains a lower proportion of Al(IV) species relative to the CC blend, indicating reduced incorporation of aluminum into C-(A)-S-H. Instead, a larger fraction of Al(VI) is associated with AFt phases. Given the voluminous nature of ettringite, this redistribution of Al can enhance space filling and contribute to pore refinement [175, 176], consistent with the trends observed in Figure 15. Furthermore, although Ht-like LDH were not distinctly resolved in the ^{27}Al MAS NMR spectra, which could be likely due to signal overlap and limited spectral resolution, their presence was confirmed by SEM–EDS mapping (Paper E).

Figure 17 shows the SEM-EDS point analysis that clarify the presence of hydrotalcite-like LDH in the VM40LS10 blend. In the Mg/Si versus Al/Si representation, OPC data remain largely confined to the main low-Mg/low-Al cluster, whereas VM40LS10 shows a distinct secondary population of points extending from this cluster and aligning along a Mg/Al of approximately 2 trendline. Because such a trend is widely used to identify Mg–Al-rich LDH-type domains in Mg-bearing cementitious systems, these data were interpreted as qualitative evidence for localized hydrotalcite-like domains in VM40LS10. Additionally, Paper E notes that XRD, TGA and FTIR alone are insufficient to unambiguously resolve this phase because LDH signatures overlap with AFm- and other Al-bearing hydrates, making the combined SEM-EDS-based interpretation particularly important. Hydrotalcite-like LDH phases are known to promote localized densification and microstructural refinement and may thus offer durability benefits, as indicated in previous studies [177–179]. Nevertheless, because quantitative hydrate analysis was beyond the scope of this study, it remains to be established how much of the available alumina is taken up by the different hydrate phases and how this partitioning influences the long term performance of the system.

Taken together, these observations suggest fundamentally different strength development mechanisms: in CC blends, strength is predominantly governed by Al incorporation into C-(A)-S-H, supplemented by AFm formation, whereas in VM blends, strength appears to arise from a composite contribution of stable ettringite, Ht, and possibly also strätlingite. Thus, comparable macroscopic strength may be achieved through distinct aluminum partitioning pathways and hydrate assemblages.

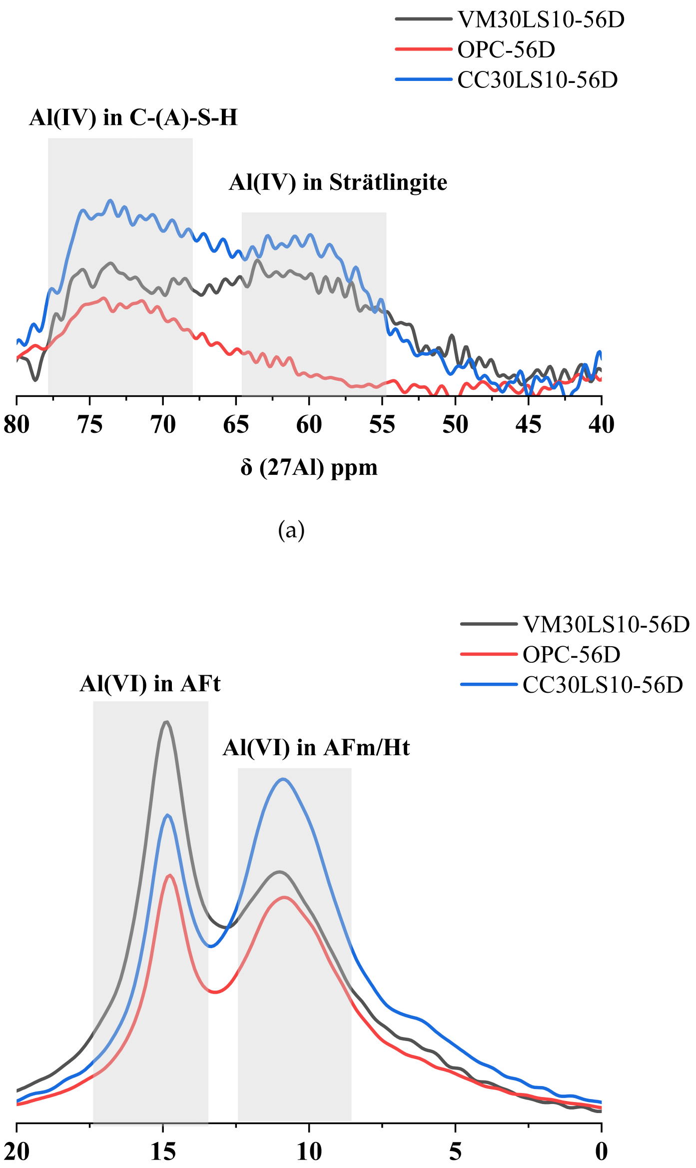
3.3.3 *Synergy with Additional Carbonates and Effect of Finer Limestone Particle Sizes*

In both systems, limestone addition did not consistently enhance strength or microstructural refinement. In the CC systems, limestone acted predominantly as a filler phase once aluminum was incorporated into C-(A)-S-H. In the VM systems, limestone effects were composition-dependent but generally secondary to SCM chemistry, with limited evidence of sustained chemical synergy. As presented in Figure 16 available reactive Alumina in both CC and VM systems preferentially get incorporated into C-(A)-S-H, AFt, and Strätlingite phases rather than become available to form carboaluminates with the available limestone. Although XRD indicates the development of CO_3-AFms, they are not sufficiently enough to contribute towards additional strength than binary SCM binders. In VM systems, results from FTIR and SEM-EDS presented in Paper E show the distribution of Al in additional systems based on the oxides present.

Additional tests were conducted using a variety of finer particle sizes of limestone (LS-M, LS-S and LS-F) presented in Table 3 compared to the LS used and reported in studies D and E. This was conducted to assess if finer particle sizes could enhance the hydration kinetics and thereby improve strength either through enhanced nucleation or chemical synergy. Figure 18 presents the compressive strength development of CC30LS10, CC40LS10, VM30LS10, and VM40LS10 prepared with LS, LS-M, LS-S, and LS-F while Figure 19 compares the reaction kinetics across selected LS sizes. The results are shown alongside OPC and the corresponding binders in which LS, LS-M, LS-S, and LS-F were substituted in the same proportions as in the CC and VM systems.

The reaction kinetics of the CC blends exhibit a higher silicate peak than OPC, which can be attributed to filler effects and accelerated precipitation of C-(A)-S-H [180], as well as additional nucleation sites provided by the activated clay and limestone [48]. The silicate hydration peak intensity increases with decreasing limestone particle size, indicating accelerated C_3S hydration [173].

The onset and intensity of the aluminate peak vary with both OPC replacement level and limestone fineness. Incorporation of finer limestone accelerates



(a)

(b)

Figure 16: ^{27}Al spectra of blends for Al(IV) coordinations corresponding to C-(A)-S-H and Strätlingite (a), and Al(VI) coordinations corresponding to AFt and AFms or Hydrotalcite (b).

C_3S hydration and promotes a higher formation rate of AFt and AFm phases, likely due to enhanced nucleation and increased limestone dissolution [48, 60, 173]. This behaviour correlates well with early-age strength development. In particular, CC30LS10(LS-F) achieves 40 ± 2 MPa at 3 days, corresponding to

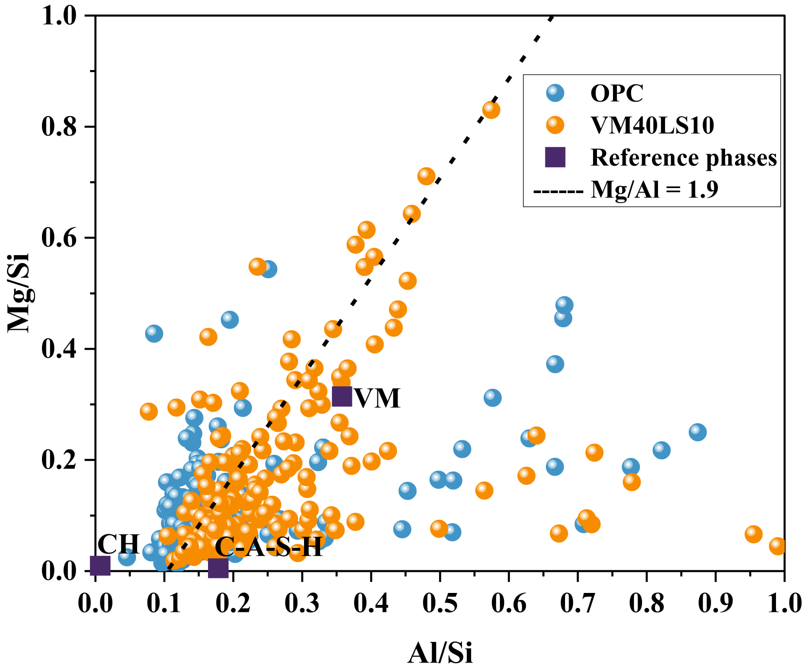
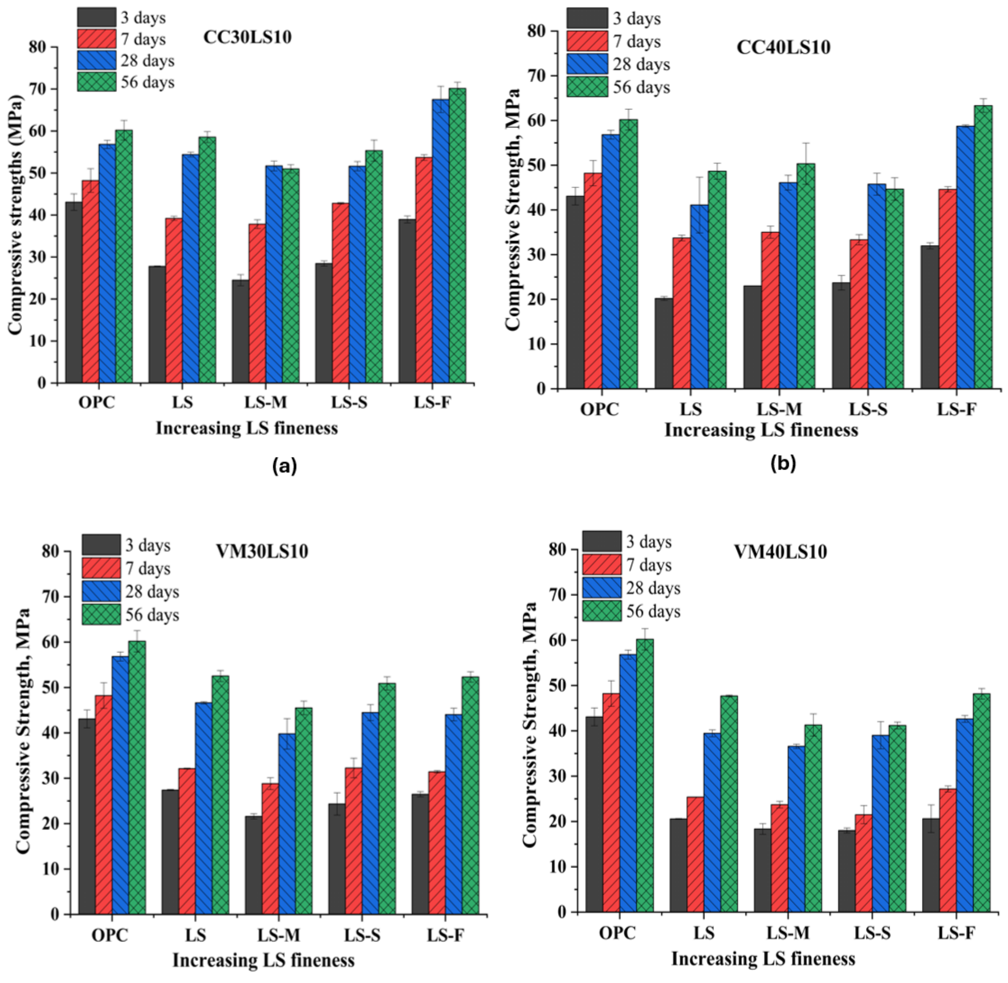


Figure 17: EDS mapping to detect Hydrotalcite like LDH phases.

90% of OPC strength, and reaches 111% by 7 days. Strength enhancement continues at later ages, reaching 119% and 116% of OPC strength at 28 and 56 days, respectively, suggesting continued pore refinement and matrix densification. At higher substitution levels, CC40LS10(LS-F) matches OPC strength after 7 days.

Compared with the corresponding binary CC blends, the ternary 40% substitution mix incorporating LS-F demonstrates higher relative strength at all ages than CC40, with increases of 43% at 3 days and 15% at 56 days. It also exhibits an 8.4% higher 3-day relative strength than the best-performing binary mix, CC30. These results indicate a possibility that enhanced densification occurs due to the presence of ultrafine particles, which contribute to refinement of the pore structure. In addition, potential chemical synergy associated with the ultra-fine particle size distribution may promote enhanced limestone dissolution [60]. However, it remains to be characterized whether the use of ultra fine LS indeed influences phase assemblage development or alters the distribution of aluminum toward octahedral coordination environments associated with AFm phases. Neverthless, even at 50% total substitution, the ternary mixes with LS-F achieve strengths comparable to OPC beyond 7 days. Compared to CC50, the CC40LS10(LS-F) blend exhibits relative strength increases by 56%, 22.7%, 20%, and 67% at 3, 7, 28, and 56 days, respectively.

For the VM systems, finer limestone incorporation leads to accelerated and more intense silicate and aluminate peaks, indicating enhanced nucleation and dilution effects. However, unlike the CC ternary systems, this kinetic enhance-



(a) (b) (c) (d)

Figure 18: Strength evolution of binders prepared with limestones of varying fineness.

ment does not translate into substantial strength gains with decreasing limestone particle size, aside from a modest improvement at 3 days. This suggests that, in VM systems, physical densification or chemical synergy with carbonates is less sensitive to limestone fineness than in calcined clay systems. This further highlights the different microstructures and chemistries in the two pozzolanic systems. If there is a chemical synergy of CC with ultra fine LS, the lack of it in VM blends could be potentially because of the lower available reactive alumina than in clay systems or more sinks for Al to incorporate, than CO_3-AFms.

At the same time, the use of LS-F to enhance strength development should be considered with caution, as it is an ultrafine precipitated limestone. At this level of fineness, such material is typically produced for specialized applications such as coatings and paints rather than for bulk construction use [181]. Moreover, its high cost (approximately 1000 euros per ton) makes it economically challenging for large-scale cementitious applications.

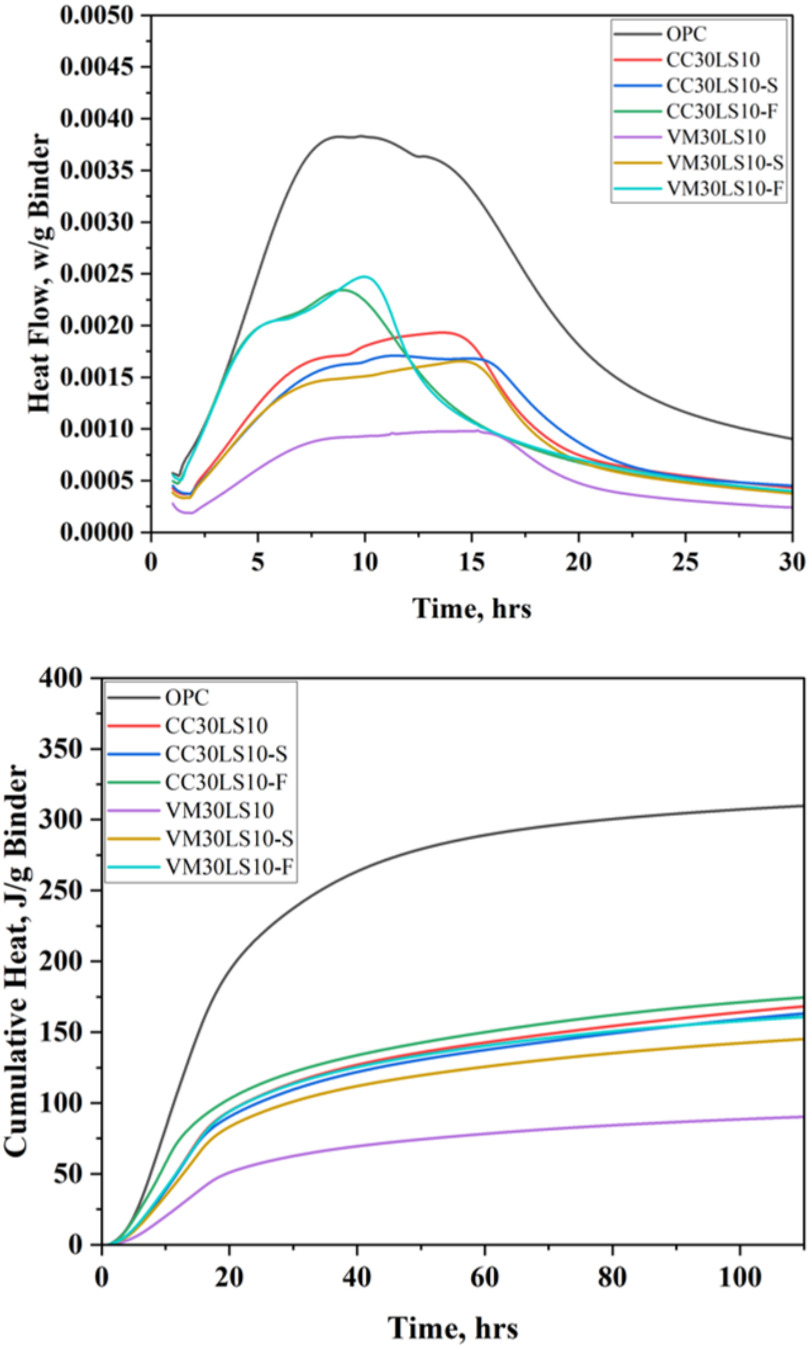


Figure 19: Reaction kinetics of CC30LS10 and VM30LS10 binders containing limestones of varying fineness.

3.4 SYNTHESIS OF HYDRATION PATHWAYS AND BINDER IMPLICATIONS

Taken together, the findings in this chapter show that activated low-kaolinite clays and volcanic materials can both function as effective SCMs based on the dataset and tests performed in this study. It was clear that hydration proceeds through both systems in different pathways. In the clay systems, the dominant mechanism is the preferential incorporation of available aluminum into C-(A)-S-H, leading to increased silicate polymerization, pore refinement, and strong later-age strength and densification even at relatively high replacement levels. In the volcanic systems, strength development and densification are slower than for clays and arise from a more distributed hydrate assemblage involving C-(A)-S-H, AFt, and Mg-bearing phases such as hydrotalcite-like layered double hydroxides, with aluminum partitioned across these wider set of sinks. This not only sets the studied VM apart from the clay, but also unique in the broader context of other reported natural pozzolans with varying compositions and origins [46, 47, 117, 125], fly ashes [64, 103], and slags [62, 167].

A second key outcome is that limestone synergy cannot be assumed from analogy with LC3-type systems. In the activated clay blends studied here, limestone did not consistently provide strong additional synergy because the available reactive aluminum was already preferentially incorporated into C-(A)-S-H, limiting its availability for extensive carboaluminate formation. In the VM blends, the composition introduces additional competition for aluminum and thereby alters the balance between filler effects, kinetic acceleration, and carbonate-related chemistry. The role of limestone is therefore system-dependent and must be interpreted together with aluminum availability and hydrate phase competition. However, the present dataset evaluated limestone additions only in 10 wt.% increments. Smaller variation in limestone content could enable a clearer differentiation of the degree of synergy in these pozzolanic systems, as reported previously for fly ash blends. [182].

Overall, Chapter 3 shows that, despite their heterogeneity and mineralogical complexity, the activated natural pozzolans were able to form viable binders once sufficient structural disorder and reactive species availability had been generated through activation. This indicates that heterogeneity, or even deposit-specific composition, should not be treated as a dismissive limitation of natural aluminosilicates. Rather it should be regarded as a material characteristic that must be understood and managed through appropriate activation strategies for greater deployment of natural SCMs.

The results from Papers D and E further show that even when properly activated, pozzolans may follow different hydration pathways and should not be grouped together too broadly. Depending on composition, activation history, and the availability of reactive elements, the hydrate assemblages formed can differ substantially, with corresponding implications for microstructural development and long-term performance. Although these investigations now open several further questions that must be addressed in future studies, they nevertheless demonstrate an important point that natural pozzolans which are heterogeneous and compositionally complex can still be developed into effective binder systems when their activation and hydration mechanisms are properly understood. In this way, the hydration investigations in this chapter complete the transition begun in Chapter 2 by linking activation-induced precursor changes to binder-level reaction mechanisms and performance.

4

CONCLUSIONS

This chapter summarises the original contributions of this PhD research and the main conclusions drawn from it. The work advances the development of naturally heterogeneous clays and volcanic materials as potential supplementary cementitious materials (SCMs). The materials investigated in this thesis represent globally abundant aluminosilicate resources, but their compositional complexity makes them less readily activable through established treatments and, consequently, less straightforward to use in cement binder systems. As a result, they have received comparatively limited attention, and their potential has remained underexplored despite their broad availability. Nevertheless, these materials possess the chemical constituents necessary for pozzolanic reactivity and, when suitably activated, are capable of forming hydrates that contribute to strength development and pore refinement. In the context of legally binding climate targets that directly affect the cement sector, together with the growing supply constraints of conventional SCMs such as slag and fly ash, it is increasingly important to improve the understanding of how such alternative resources can be activated and how they behave during hydration in blended cementitious systems. To address this need, the thesis formulated five research questions focused on the relationships between activation treatments, physicochemical properties, reactivity, hydration, and microstructural evolution. The following sections present these research questions together with the conclusions drawn from the studies undertaken in this PhD.

1. **RQ1: Can low-kaolinite clays and mineralogically diverse volcanic materials be effectively activated using common thermal or mechanochemical methods to achieve meaningful pozzolanic reactivity?**
    - Both low-kaolinite clays and mineralogically diverse volcanic materials could be activated to achieve improved pozzolanic reactivity, but the choice and effectiveness of the activation route depended strongly on precursor mineralogy. The low-kaolinite clays consisted mainly of mixed 2:1 phyllosilicates with accessory non-clay phases, whereas the volcanic materials comprised mainly feldspar or glass bearing assemblages with variable initial amorphous contents and chemical compositions. As clays and volcanic materials host their reactive phases in different structures, they followed distinct activation - reactivity pathways.
    - For the low-kaolinite clays, a combined thermal (TA) and mechano chemical activation (MCA) could bring the reactivities of both low kaolinite heterogenous clays to moderate reactive levels. Among studied parameters, TA–MCA20 produced the highest reactivity im-

provements, with increases of up to 374% relative to TA alone and 127% relative to MCA alone. This suggests that, in these heterogeneous low-grade clays, the individual application of TA or MCA may be insufficient to fully enhance pozzolanic performance.

- For the diverse volcanic materials, MCA alone was highly effective. Across four mineralogically distinct Icelandic volcanic materials, a common MCA regime of ball/powder ratio 25 and milling speed 500 rpm systematically shifted the materials from near-inert reactivity (40–60 J/g SCM) toward moderate and high reactivity. In the strongest case, MR3 reactivity increased from 56 to 350 J/g SCM, while one volcanic material exceeded 400 J/g SCM after 20 min of MCA, corresponding to a highly reactive pozzolan.
- Overall, the results demonstrated that within each family of heterogenous pozzolans, common activation techniques can successfully enhance the reactivity but activation parameters are not transferable without mineralogical context across two families. Low-kaolinite clays required TA–MCA to reach maximum reactivity, whereas volcanic materials responded strongly to MCA alone.

2. **RQ2: How do activation techniques modify mineralogy, particle sizes, specific areas and chemical structures of Al–Si networks and how do these changes correlate with measured reactivity?**
    - Activation modified mineralogy, particle size distribution, specific surface area, and the chemical structure of the Al–Si network in both precursor families, and these changes correlated directly with measured reactivity.
    - For the low-kaolinite clays, TA–MCA was the most effective because it combined the strongest particle and surface refinement with the highest mineralogical and structural disorder. XRD confirmed the greatest loss of phyllosilicate crystallinity and the highest degree of amorphization, with values up to 124% higher than TA and 84% higher than MCA. Simultaneously, BET-SSA increased by up to 374% relative to TA and 158% relative to MCA, and these changes correlated with the strongest reactivity improvements.
    - Further spectroscopic analyses demonstrated that in the representative low-kaolinite clay, TA, MCA, and TA–MCA modified the Al–Si framework through different atomic-scale pathways. TA was mainly reorganisation-dominated, MCA fragmentation-dominated, and TA–MCA caused the greatest network disruption. Structural disorder increased systematically from the unactivated state to TA, MCA, and finally TA–MCA.
    - ^{27}Al MAS NMR showed that TA promoted conversion of octahedral Al into more ordered tetrahedral environments, while MCA increased distorted Al environments through strain and local heterogeneity. TA–MCA caused the strongest disruption, with nearly

complete loss of residual Al(VI), the highest fraction of distorted Al(VI), and the broadest Al resonances.

- ^{29}Si MAS NMR showed that TA increased Si–O–Al connectivity, MCA promoted cleavage and depolymerisation of Si–O–Al linkages, and TA–MCA produced a more decoupled and disordered aluminosilicate network. Overall, it was found that activation changed the local Al–Si coordination environments in ways that correlated well with reactivity, with TA–MCA producing the highest atomic-scale disorder and the strongest reactivity enhancement in the studied clay.
- In the volcanic materials, MCA produced systematic reductions in particle size, increases in BET-SSA, and increases in the degree of amorphization, despite the mineralogical diversity of the precursor set studied. The most pronounced response showed a decrease in D50 from 37 µm to 9 µm, an increase in BET-SSA from 4 to 13 m^2/g, and an increase in average degree of amorphization from 70 to 83%, which corresponded directly to strong increases in MR3 reactivity.
- Although the two material families differed in mineral structure and activation requirements, their response to treatment could still be evaluated within a common framework. In both cases, greater amorphization, along with particle size refinement and increased SSA, correlated well with calorimetry-based reactivity, enabling comparison between heterogenous low-kaolinite clays and volcanic pozzolans.

3. **RQ3: How do activated clays and volcanic materials perform in blended cements in terms of strength and pore structure development relative to OPC?**

   - Combinedly activated low-kaolinite clay blends showed competitive performance relative to OPC, particularly in binary systems and at replacement levels up to 40%. Binary blends with 20–40% activated clay reached up to 125% of OPC strength at 56 days, indicating that suitably activated clays can not only compensate for clinker dilution but also promote improved later-age performance.
   - This strength development in the clay blends was closely linked to progressive pore refinement. Higher clay contents generally led to denser microstructures, with the 30% binary blend showing a 42% reduction in total porosity at 56 days. Refinement was especially pronounced in the gel pore range, consistent with continued hydrate formation and matrix densification.
   - Limestone-containing clay blends showed slower early strength development. Although strength continued to increase at later ages, the ternary mixes did not reach the same strength level as the corre-

sponding binary clay blends, indicating that limestone addition was less beneficial for strength development in the studied clay systems.

- Activated VM blends also showed promising performance relative to OPC, although their development was somewhat different from the clay systems. VM30 reached strength comparable to OPC at 56 days, while VM40 still achieved about 92% of OPC strength, showing that relatively high substitution levels remained feasible.
- In the VM blends, pore structure evolution was characterised by increased gel pore volumes relative to OPC, together with continued reduction of capillary and macro pores over time. This indicates that, although the VM systems developed a different pore size distribution from OPC, hydration products progressively refined and densified the matrix and supported later-age strength gain.

4. **RQ4: What hydration mechanisms govern these blends, particularly regarding incorporation of aluminium into C-(A)-S-H or AFm phases, and how does this influence synergy with limestone**?

   - In the activated clay blends, hydration was governed primarily by progressive pozzolanic reaction, CH consumption, and the development of Al-rich C–(A)–S–H, with additional formation of carbonate-containing AFm phases in limestone-bearing systems. The combined microstructural evidence showed that Al released from the activated clay increasingly entered tetrahedral environments over time and was incorporated mainly into the C–(A)–S–H structure.
   - ^{27}Al NMR showed that Al in the clay blends remained predominantly tetrahedral at later ages, with only minor octahedral Al. This suggests that Al was incorporated mainly within the C–(A)–S–H network rather than being consumed predominantly in separate AFm-type phases. The resulting increase in Al uptake and silicate chain development in C–(A)–S–H contributed strongly to pore refinement and later-age strength.
   - In the clay systems, limestone modified the hydrate assemblage and delayed early strength development, but no clear strength advantage over the binary blends was observed. This suggests that, under the studied conditions, the additional AFm-related reactions did not translate into a stronger synergistic effect than the direct contribution of activated clay to C–(A)–S–H formation and matrix densification.
   - In the VM blends, hydration followed a more complex pathway than in the clays. The hydrate assemblage included C–(A)–S–H, AFt, possibly strätlingite, and Mg–Al LDH-type phases, while hydrogarnet formation remained limited or below detection. Thus, Al released during hydration was not directed mainly into one hydrate family, but was distributed among several competing reaction products.

- The VM systems showed no clear limestone synergy among the binders studied. The likely reason is that reactive Al availability was limited and also competed with Mg-bearing phases, which restricted the formation of carbonate-AFm phases. Under these conditions, limestone appeared to act mainly as a filler and nucleation aid rather than as a strong chemical enhancer.
- Overall, the hydration mechanisms differed markedly between the two precursor families. The clay blends were governed mainly by Al incorporation into C–(A)–S–H with limited AFm contribution, whereas the VM blends showed more distributed Al uptake across multiple hydrates. These differences help explain why limestone was less synergistic in the studied systems than might be expected in more Al-rich SCM blends.

5. **RQ5: In MgO and Fe_2O_3 containing volcanic SCM systems, how is alumina distributed among C-(A)-S-H, CO_3-AFm phases, Mg and Fe-based hydrates, and how does this partitioning affect mechanical and pore structure evolution?**

   - In the MgO-containing VM systems, alumina did not follow a single dominant incorporation pathway. Instead, it was partitioned among several competing sinks, including C–(A)–S–H, AFt, AFm, possibly strätlingite, and Mg–Al LDH-type hydrates. This distinguishes the VM systems from many conventional aluminosilicate SCMs, in which Al uptake is often dominated by fewer hydrate phases.
   - ^{27}Al MAS NMR showed that part of the Al was incorporated into the C–S–H structure, consistent with the formation of C–(A)–S–H. However, the presence of Mg introduced an additional sink in the form of hydrotalcite-like LDH phases, which likely reduced the extent to which Al could be incorporated into C–(A)–S–H or carbonate-AFm phases.
   - No strong evidence of extensive CO_3-AFm formation was found in these VM systems, indicating that carbonate-bearing AFm was not a dominant Al sink. This helps explain the limited limestone synergy observed, since the available Al was distributed across several competing hydrates rather than being preferentially directed into carboaluminate formation.
   - Mg–Al LDH phases appeared as localised Mg-rich domains and likely contributed to matrix densification and stiffness. Their formation, together with AFt and possibly strätlingite, corresponded with continued reduction in capillary and macro pore volumes over time, even though gel pore volumes remained higher than in OPC.
   - This distributed alumina partitioning had important consequences for performance. Because Al was shared among C–(A)–S–H and other Mg-bearing hydrates rather than concentrated in a single strengthening phase, the VM blends developed strength more gradually

than the best-performing clay blends. Nevertheless, the continued formation of these hydrates supported ongoing pore refinement and enabled VM30 to reach OPC-equivalent strength by 56 days.

- With respect to Fe-bearing hydrates, their role could not be resolved clearly within the present dataset. The main identifiable additional Al sink was the Mg–Al LDH-type phase, and this appears to be the dominant feature controlling alumina partitioning and its consequences for hydrate development in the studied MgO-containing VM systems.

4.1 LIMITATIONS

The following bullets summarize some limitations of the study:

1. Activation parameters are not comprehensive and mostly bounded by practical lab and time constraints. All combinations were not conducted that limits understanding of if different settings permitted a more energy efficient method.

2. Scale up for activation have not been investigated. Planetary milling and lab-scale processing generate impact/shear fields that do not map one-to-one to industrial mills; performance trends are robust, but the quantitative "best" MCA duration or energy will change at production scale.

3. Grinding aids and milling losses were not assessed. No grinding aids or process control agents were evaluated during mechanochemical activation, and mass losses were observed during MCA of clays (e.g., adhesion of fine powder to jars/balls and handling losses). This introduces uncertainty in the effective energy input per unit mass and in scalability, since industrial milling typically relies on grinding aids to control agglomeration, improve throughput, and reduce losses.

4. Very early-age strength effects at 1 day was not focussed as the focus was more on the evolution for the hydration studies. This limits conclusions on ultra-early kinetics (e.g., initial set, early aluminate/sulfate balance, and the practical feasibility of high replacement levels where formwork striking or rapid construction schedules require 24-hour strength.

5. Performance metrics focus on strength and porosity. Autogenous/drying shrinkage, creep, or cracking sensitivity of the new binders, which are properties that may matter for structural use at higher replacements were outside the scope of this work.

6. NMR selection depth and representativeness. ^{27}Al and ^{29}Si MAS NMR provides high-value mechanistic insight but was applied to selected representative blends and ages; full time-resolved NMR across all compositions was not feasible, so some partitioning trends are inferred from representative points only.

7. ^{29}Si MAS NMR was not performed for the VM blends. In the VM systems, NMR work focused on ^{27}AlAl MAS NMR to resolve Al partitioning among competing hydrate sinks and the relation of that on bulk performances, while quantitative ^{29}Si MAS NMR (e.g., Q-species deconvolution, mean chain length of C-(A)-S-H) was outside the scope. As a result, changes in silicate polymerisation and C-(A)-S-H chain development in VM blends could not be directly quantified and can provide a complementary link between C-(A)-S-H structure and pore refinement.

8. Identified hydrate phases in the blends and he performance implications of specific hydrates were not quantified and were interpreted based on established literature. For example, AFts, strätlingite are generally associated with space-filling and matrix densification and hydrotalcite is known for enhanced contribution to chloride binding but their volume fraction and direct contributions were outside the scope of this work.

9. The hydration study was based on a statistically designed mix proportion matrix, but the step size adopted for SCM additions may be broad to resolve possible synergies with limestone that might occur at lower incremental addition levels.

5

DEVELOPMENTS

This chapter first highlights the key scientific and methodological developments achieved in the thesis.

5.1 DEVELOPMENTS AND CONTRIBUTIONS

1. Evaluated a combined thermo-mechanochemical activation (TA-MCA) methodology for mixed natural low-grade clays.
   a) Paper A established this as a promising alternative route for improving the pozzolanic reactivity of heterogeneous natural low-kaolinite clays, which are difficult to activate comprehensively through standalone TA or MCA treatment. This challenge arises from their mineralogical heterogeneity and the contrasting responses of coexisting 1:1 and 2:1 clay phases to calcination and milling. Earlier studies had generally shown TA to be more suitable for 1:1 clays, whereas MCA could be effective for certain single phase or dominating 2:1 clays. The present work advanced this understanding by showing that a TA-MCA approach can successfully bridge this divide in mixed clay systems coupling dehydroxylation of heat-responsive phases with mechanochemical disruption and surface activation of the remaining mineral structure. In this way, the study provides suitable activation route for heterogeneous low-grade clays which otherwise remain difficult to valorise.
   b) Importantly, a wider relevance of this work is reflected in the similar combined activation approaches that were subsequently reported for clays from different geographical origins, with several of these later studies citing the present work [183–189]. These subsequent studies from across different continents indicate that the approach reported in Paper A is not confined to the specific Swedish clays investigated within this PhD, but has broader significance for the valorisation of heterogeneous, low-reactive clay resources.
2. First atomic-scale, mechanistic explanation of why combined TA-MCA works on low kaolinitic, heterogneous clays, compared to TA or MCA conducted individually.
   a) As far as is currently known, the work presented in Paper B provides one of the first quantified mechanistic explanations of how TA, MCA, and combined TA–MCA modify Al–Si coordination environments and framework disorder in low-kaolinite heterogeneous clays.

    It shows that TA–MCA induces atomic-scale changes in the aluminosilicate network that represent a distinct activation pathway. The study further demonstrates that the statistical descriptors of these network changes correlate strongly with measured reactivity. This indicates that the comparatively superior performance of TA–MCA does not arise solely from particle or surface refinement, but from deeper mechanistic modification of the clay structure itself.

    b) The activation–structure–reactivity relationships established in this study support the development of more generalisable activation strategies for mixed-phase clays and offer a basis for extending similar approaches to other heterogeneous pozzolans

3. Developed and demonstrated potential of MCA across diverse, intrinsically low reactive volcanic materials.

    a) Demonstrated a systematic validation that MCA can be applied as a general activation route for diverse volcanic materials, not just case-specific compositions.

    b) The results of this thesis demonstrate that a common interpretation framework, correlating degree of amorphization, particle size distribution, specific surface area, and calorimetric reactivity, can enable systematic comparison across diverse VMs. This can provide a transferable basis for evaluating activation effectiveness. The relevance of this approach is further reflected in its adoption in subsequent studies, some of which build upon and refer to the present work [135].

4. Defined a statistically supported approach for designing representative blends and assessed them for evolution of strength and porosity.

    a) The key development is not the statistical tool itself as it has been used previously in several research (to also design binders). The main contribution is mechanistic interpretation and the realistic binder design range it helped to define for the particular combined activated, low kaolinte clay.

    b) This represents an important development, as binder substitutions and proportions established for high-kaolinite clays are not directly transferable to mixed-mineralogical systems or to other pozzolanic materials such as VMs. The approach provides a useful starting framework for exploring the feasible design space of new binders and assessing their feasibility for application.

5. Resolved Al pathways in low alumino-silicate clays and VMs.

    a) Previously, it was understood that low-alumina clays exhibited no measurable synergy with limestone, which was attributed to their limited aluminum availability. The combined ^{29}Si and ^{27}Al NMR approach enabled clarification of the reaction pathways in such systems by quantifying C-(A)-S-H polymerization alongside the concurrent increase in other tetrahedrally coordinated aluminum. The results indicate a preferential incorporation of the limited available Al into C-(A)-S-H rather than into AFm phases.

b) It is clarified from the study on VM hydration that Al partitioning in low alumina pozzolans is dependant on the composition of the SCM and availability of other reactive species that can take up Al.

6

FUTURE SCOPE

The findings presented in this thesis contribute to a deeper understanding of activation–reactivity relationships in naturally heterogeneous clays and volcanic materials, and how they influence hydration evolution in binders containing activated pozzolans. At the same time, the work has brought to light several new questions that extend beyond the immediate scope of the present study. This is a natural outcome of scientific inquiry, which proceeds iteratively. The results obtained here therefore provide not only answers to the research questions posed, but also a framework from which further mechanistic, compositional, and performance-related studies can be developed. This chapter accordingly outlines strategic directions for future research, with the following points summarizing some key areas:

1. Investigating how Al-enriched C-(A)-S-H in activated clay binders and potentially hydrotalcite-like phases in VM systems contribute to chloride adsorption and transport resistance in the absence of significant AFm formation.

2. Quantifying carbonation kinetics and depth progression in low or portlandite - depleted matrices as a function of altered pore structure and hydrate phase assemblage evolution.

3. Investigating the freeze–thaw durability of low-portlandite pozzolan based systems by evaluating pore size distribution, degree of saturation, and critical saturation thresholds, including performance under both internal damage and surface scaling conditions.

4. Assessing the compatibility of air-entrainment with modified binder chemistries and examine how ongoing microstructural refinement influences long-term frost resistance in blended cement systems. Reduced portlandite content could alter internal moisture buffering capacity and pore solution chemistry, potentially influencing ice formation pressures and scaling resistance.

5. Evaluating sulfate resistance by examining the stability of C-(A)-S-H, AFt/AFm phases, and Mg-bearing hydrates under external sulfate exposure, and determining how altered aluminate and carbonate equilibria influence expansion, phase transformation, and long-term durability.

6. Exploring the implications of increased Al incorporation in C-(A)-S-H associated with Ca depletion in low-clinker systems, and assessing whether design principles from lime-based mortar systems could inform strategies to enhance long-term phase stability and durability under reduced portlandite conditions.

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