THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING IN ARCHITECTURE AND CIVIL ENGINEERING

Characterization, Activation and Reactivity of Natural Pozzolans for Use as Supplementary Cementitious Materials

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The cover image displays SEM images of volcanic material (pumice), contrasting un-active particles on the left with activated ones on the right, achieved through mechanochemical grinding.

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To all who have taught me, thank you

Preface

This thesis is submitted to Chalmers University of Technology in line with the requirements for the degree of Licentiate. The work entailed in this thesis has been conducted at the Department of Architecture and Civil Engineering, under the supervision of Arezou Babaahmadi (Assistant Professor, Building Materials group, Chalmers), Liming Huang (Post-doc, Building Materials, Chalmers), Klaartje de Weerdt (Professor, Department of Structural Engineering, Norwegian University of Science and Technology (NTNU)), and Luping Tang (Professor, Building Materials, Chalmers). The examiner of the PhD is Holger Wallbaum (Professor, Building Technology, Chalmers). The work has been majorly financed by the Swedish Research Council, Formas under the project name of *New era for cement replacement materials: Importance of service life design* (NewDurCem with grant number:FR-2020/0008). This work is also partially connected and funded by Vinnova (Sweden's Innovation Agency), Grant number: 2021-01053, under the project: *Towards a climate neutral and resource efficient soil stabilization additive* (the work is carried out within the strategic innovation program InfraSweden2030, a joint initiative by Vinnova, Formas and the Swedish Energy Agency). Finally, this thesis forms a foundation for the project: *Evolution of pozzolan incorporated concrete: resistance to carbonation* (Carbo-crete), financed by Family Thomas Foundation, from which certain experimental analysis are funded.

The broader PhD research focuses on investigating the durability aspects of locally available low-carbon cement alternatives, mainly in terms of chloride transport and frost. As a first step towards this aim, exploration of the pozzolanic properties of potential supplementary cementitious materials (SCMs) was conducted. This could then facilitate the development of optimized mix designs that could be used for assessing durability parameters. This research began with an examination of clay as a primary material, inspired by insights from a recently concluded RISE report [1], which assessed the potentials of clays from various regions in Sweden. Subsequently, for this study, two heterogenous clays were sourced from sites that were accessible for excavation.

During the investigation of clay pozzolanicity, it became evident that the selection of activation treatments played a crucial role in modifying physicochemical parameters, thereby influencing reaction kinetics observed in pozzolanicity tests. Given the inherent compositional heterogeneity and subsequent lower natural reactivity observed in the clays under study, it became essential to explore a variety of activation methods and their impact on physical and chemical parameters. This exploration was crucial for achieving the desired reactivities necessary for realistic cement substitution. Thus, the current thesis delves into the intricate interplay

among activation mechanisms, mineral compositions, particle size distributions, and surface areas to elucidate the factors influencing achievable reactivity levels.

Subsequently, the research expanded to include an examination of other natural pozzolans accessible to the Swedish construction industry, notably volcanic materials from Iceland, which have garnered increasing interest due to their abundance, large reserves, and convenient transportation options [2, 3]. Similar to the investigation on clays, the study examined the dependencies between activation parameters, physicochemical properties, and reactivity in four volcanic materials sourced from Iceland. The objective was to comprehensively understand these relationships to inform future explorations in the field.

The thesis primarily compares the findings from two manuscripts: one (Paper A) detailing investigations on clay, accepted for publication, and the other (Paper B) covering studies on volcanic materials, currently completed for submission.

Acknowledgments

I want to express my gratitude to a number of individuals who have been instrumental in getting me through the halfway point of my PhD. First and foremost, I thank Arezou for taking me into the fold and for her consistent efforts to make a better researcher and academic of me. Thank you for continually having my back, genuinely caring about my development, and being there for me — even during the oddest of hours. I also express my sincere appreciation to my daily supervisor Liming, for always supporting me and enabling me to do my best.

I am very grateful to my co-supervisors Klaartje and Tang, for their guidance and encouragement. Like several other young researchers across our domain, I look up to both of you as my role models. Special thanks to my examiner Holger for not only his ready assistance with formal requirements, but also for sharing his expertise on aspects of sustainability. His reminders to involve these aspects within the broader scope of my work have been enriching. I like to thank Sigurdur Erlingsson and Ingemar Löfgren for their support and to all the experts I have had the honour to collaborate as co-authors.

I would like to thank my division head Angela Sasic Kalagasidis for taking active interest in my overall growth and well-being. Thank you for also driving efforts to ensure that our BT laboratory is staffed with both the right personnel and instruments. A note of thanks to Stefan Nilsson, our previous manager, for his invaluable support in helping me settle into the workplace when I joined in the summer of 2021.

I extend my gratitude to the staff of the building materials lab at RISE, Borås, with special acknowledgment to Gilles, Emily, Ojas, and Natalie, for their invaluable assistance and expertise in conducting several crucial experiments for the study. Additionally, I thank Jennie from ALS Global at Piteå for the efficient coordination in conducting essential tests. I extend my gratitude to Bruno, our lab research engineer at Chalmers, for bringing exceptional organization to our lab and for his attentive care and understanding of my lab requirements. Additionally, I would like to thank Mohammad and Suriya, our former research assistants, whose assistance with material preparations was crucial in meeting my deadlines.

I would thank all the students whom I have had the privilege to supervise. Each of you has been instrumental in my growth as a more effective communicator and aspiring educator.

Many thanks to the wonderful people I am fortunate to share my workplace with. Special thanks to Jan, my very first PhD colleague for being homely at all times. I'm grateful to Xinyue for her constant support, checking in on my progress, and introducing me to the delights of hotpot. Divia, thank you for

keeping our spirits high with mandatory celebration targets after reaching paper milestones together. To Liming, Birhan, Juan, Sahar, and Baodong, I appreciate the memorable moments we've shared both in and out of the lab, and I look forward to many more. A heartfelt thanks to my friends from India, Netherlands, and Gothenburg for simply being there, caring, and the laughs when needed.

My family is my rock - I cannot be more grateful for them in my life. Thank you for being my biggest enablers and empowering me to just follow my dreams, no matter the circumstances. I love you all deeply. And to Ritu, beyond helping me conquer the toughest of Latex errors, I am grateful every day for the priceless joys you bring into my life. Thank you for being my sanctuary.

Characterization, Activation and Reactivity of Natural Pozzolans for Use as Supplementary Cementitious Materials

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Abstract

Supplementary cementitious materials (SCMs) represent one of the most practicable ways to reduce the negative environmental impact of cement. Natural pozzolans like clays and volcanic materials (VMs) offer promising alternatives to industrial by-products such as blast furnace slags and fly ashes, whose availability cannot meet the growing demand for SCMs globally. However, comprehensive implementation of these pozzolans in the built sector, raises unanswered questions. One key concern is understanding the activation requirements of pozzolans with diverse compositions, which can impact their physicochemical properties and reactivity. In this context, the present thesis investigates how commonly used activation methods affect particle size, surface areas, and chemical properties, influencing the reactivity of multiple samples of heterogeneous clays and volcanic materials from the Nordic region, differing in mineralogical characteristics.

In the context of heterogeneous natural clays, it is frequently noted that either traditional thermal activation (TA) or mechanochemical activation (MCA) can fully dehydroxylate minerals, a process crucial for optimal clay reactivity. However, findings from the current investigations highlight that combining these methods brings notable changes in key parameters. Notably, integrating 20 mins of MCA at 500 rpm with prior thermal treatment at 800°C led to 158% increase in specific surface area compared to MCA on un-calcined clays. This was associated with a 127% improvement in reactivity levels, when compared to the levels possible from traditional activations.

Regarding volcanic materials (VMs), prolonged MCA durations of up to 20 mins demonstrate significant modifications in physical and chemical parameters. Compared to 5 mins of MCA at 500 rpm, 20 mins of MCA resulted in a notable reduction of up to 76% in D50, a substantial increase of up to 225% in surface area, and a rise of up to 47% in amorphous content, accompanied by observable increases in reactivity levels.

Keywords: Pozzolans, Activation, Reactivity, SCMs, Clays, Volcanic Materials

Sammanfattning

Cement ersättningsmaterial representerar en av de mest praktiska sätten att minska cementets miljöpåverkan. Naturliga puzzolaner som leror och vulkaniska material (VMs) erbjuder lovande alternativ till industriella biprodukter som slagg från masugnar och kol flygaska, vars tillgänglighet inte kan möta den växande efterfrågan på SCM globalt. Emellertid höjer en omfattande implementering av dessa puzzolanser i byggsektorn obesvarade frågor. En nyckelfråga är att förstå aktiveringskraven för puzzolanser med varierande sammansättningar, vilket kan påverka deras fysikokemiska egenskaper och reaktivitet. I denna kontext undersöker den nuvarande avhandlingen hur vanligt förekommande aktiveringsmetoder påverkar partikelstorlek, specifik yta och kemiska egenskaper, vilket påverkar reaktiviteten hos heterogena leror och vulkaniska material.

I samband med heterogena naturliga leror noteras det ofta att antingen traditionell termisk aktivering (TA) eller mekanokemisk aktivering (MCA) helt kan dehydroxylera mineraler, en process som är avgörande för optimal lerreaktivitet. Emellertid belyser resultaten från denna studie att kombinera dessa metoder medför märkbara förändringar i nyckelparametrar. Särskilt integrering av 20 minuters MCA vid 500 rpm med föregående termisk behandling vid 800°C leder till en signifikant ökning med 158% av specifik yta jämfört med MCA på okalcinerade leror. Denna förbättring var assoierade med en ökning med 127% i reaktivitetsnivåer. När det gäller vulkaniska material (VMs) visar förlängda MCA upp till 20 minuter betydande modifieringar. Vid 500 rpm resulterade 20 minuters MCA jämfört med 5 minuter i en betydande minskning med upp till 76% i D50, en betydande ökning med upp till 225% av den spesifika ytan och en ökning med upp till 47% av amorft innehåll, åtföljt av observerbara ökningar av reaktivitetsnivåer.

Acronyms

OPC:	Ordinary Portland Cement
CO_2:	Carbon Dioxide
AF:	Alternative Fuels
CCS:	Carbon Capture and Storage
SCM:	Supplementary Cementitious Materials
VM:	Volcanic Materials
CH:	Calcium Hydroxide
LC3:	Limestone Calcined Clay Cement
MCA:	Mechanochemical Activation
TA:	Thermal Activation
TA-MCA:	Combined thermal and mechanochemical activation
R3:	Rapid Relevant and Reliable (reactivity) test
MR3:	Modified Rapid Relevant and Reliable (reactivity) test
B/P:	Ball to Powder ratio
NC:	Nörrköping clay
SC:	Skåne clay
LS:	Limestone
PCE:	Polycarboxylate Ether
XRD:	X-Ray Diffraction
FTIR:	Fourier Transform Infrared spectroscopy
ATR-FTIR:	Attenuated Total Reflectance-Fourier Transform Infrared
ICP-AES:	Inductively coupled plasma atomic emission spectroscopy

TGA:	Thermogravimetric Analysis
BET:	Brunauer–Emmett–Teller
SEM:	Scanning Electron Microscopy

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List of Publications

This thesis is based on the following publications:

[A] **Amrita Hazarika**, Liming Huang, Arezou Babaahmadi, , "Characterization, Activation, and Reactivity of Heterogenous Natural Clays". *Manuscript accepted for publication in Materials and Structures.*

[B] **Amrita Hazarika**, Liming Huang, Sigurdur Erlingson, Klaartje de Weerdt, Ingemar Löfgren, Sahar Iftikhar, Arezou Babaahmadi, "Characterization, Activation and Reactivity - A Case Study for Nordic Volcanic Materials for Application as Supplementary Cementitious Materials". *Manuscript to be submitted.*

Co-authored publications not included in this thesis are:

[1] **Amrita Hazarika** and Arezou Babaahmadi. 2023, "Reactivity of Mixed Layer Clays - The Effect of Polycarboxylate Based Superplasticizers on Effective Particle Size Distributions.". *In: International RILEM Conference on Synergising Expertise towards Sustainability and Robustness of Cement-based Materials and Concrete Structures.* RILEM Bookseries, vol 44, Springer, Cham. DOI: https://doi.org/10.1007/978-3-031-33187-9_29.

[2] Raine Isaksson, Max Rosvall, Arezou Babaahmadi, Apollo Buregyeya, **Amrita Hazarika**, Joseph Mwiti Marangu, Kolawole Olonade, Swaminathan Ramanathan, Anthony Rucukye, and Luca Valentini. 2023, "Supplementary Cementitious Materials in Building Blocks—Diagnosing Opportunities in Sub-Saharan Africa". *Sustainability,* vol 15 (7), MDPI, DOI: https://doi.org/10.3390/su15075822.

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Part I

Overview

CHAPTER 1

Introduction

This chapter aims to contextualise the increasing interest in supplementary cementitious materials, specifically natural clays and volcanic materials. It positions these natural pozzolans as potential substitutes for cement, contingent upon a thorough understanding of their properties and behavior. The chapter reviews the existing research on these materials, highlighting the areas that still lack comprehensive understanding. It identifies unanswered questions related to the full utilization of these materials, forming the basis for research questions. The chapter wraps up with discussions on the experimental research framework for the current licentiate work, as well as detailing the thesis outline, objectives, and hypotheses.

1.1 Context

The dawn of this decade revealed a critical seismic shift as the worldwide anthropogenic mass, primarily driven by cement-based constructions, exceeded the cumulative biomass of the entire plant kingdom [1, 2]. As of the onset of 2024, the annual production of Ordinary Portland Cement (OPC) is projected to reach approximately 4.8 billion metric tonnes within the next two years - a quantity nearly double the global annual consumption of food [3, 4]. This overwhelming demand for cement is driven by infrastructure-focused stimulus initiatives in

mainly low to middle-income nations, the rapidly rising global population, urbanization trends, and extensive restoration efforts for deteriorating infrastructure in affluent economies. In terms of longevity, versatility, cost-effectiveness, and overall reliability, cement remains unparalleled, explaining why the demand for cement is projected to continue to surpass that for any other building material [5].

However, for each metric ton of cement manufactured, there is a release of up to 622 kilograms of carbon dioxide (CO_2) [6]. Consequently, the cement industry stands as the third-largest contributor to global anthropogenic carbon dioxide emissions, accounting for 5% to 8% of the total [7, 8]. This implies the need for urgent interventions and innovations to align global demand with sustainability concerns. Through a specific calculation, meeting the objectives delineated in the Paris Agreement on climate change requires the cement sector to achieve a minimum 16% reduction in its annual emissions by the year 2030[9]. However, accomplishing this is a formidable task, given that no single available mitigation strategy can fully realize the aforementioned objective.

50% carbon emissions from cement production come from the calcination of limestone - the key ingredient in cement, at temperatures of 1400° C. Complementarily, 40% of emissions emanate from the combustion of fossil fuels in cement kilns, with an additional 10% attributed to transportation and electricity consumption, as outlined by [10]. In accordance with the consensus among global sustainability researchers and think tanks, achieving sustainability targets in the cement industry hinges on addressing three crucial facets: enhancing energy use efficiency and incorporating low-carbon or alternative fuels (AF), adopting innovative technologies like carbon capture and storage (CCS), and diminishing the clinker-to-cement ratio through OPC substitution with supplementary cementitious materials (SCMs) [6, 7, 10, 11].

The first two mitigation strategies faces substantial challenges that hinders immediate application. In the context of alternative fuels, the challenges include adverse effects on combustion processes that may potentially alter the cement chemistry of the new clinker, and also lead to reduced clinker production capacities [12]. Additionally, the continuous absence of thorough research and the potential rise in marginal costs for clinker production linked to CCS technologies suggest that the avenues towards decarbonizaton of cement cannot as yet, fully rely on it [13]. Alternatively, partial substitution of OPC clinker emerges as a successful and relatively well-established strategy for decarbonizing cement production. Notably, it is less reliant on technological upgrades at the production level, thus facing lower barriers to industrial applications and enjoying higher commercial acceptance compared to other innovative technologies. Significant ef-

forts in this domain have aimed to achieve a remarkable reduction in OPC clinker by incorporating variety of SCMs over the past decades [14]. These materials, exhibiting behavior similar to traditional cements when added to water and a lime source, do not involve the calcination of limestone to exhibit cementitious properties. This approach targets the elimination of a substantial share of the 50% of CO_2 emissions generated during the cement manufacturing process. Given the practicality of utilizing alternative cementitious materials as a mitigation strategy, both research interest and public funding have experienced rapid acceleration over the years in the realm of SCMs. Fig 1.1 shows the steadily increasing number of peer reviewed research interest on the topic of SCMs in contrast to that of AF and CCUS. On the other hand, in financial terms, by 2020, the global market for SCMs was valued at 20.1 billion USD, and it is projected to reach 39.9 billion USD by 2030, growing at a CAGR (Compound Annual Growth Rate) of 7.2% from 2021 to 2030 [15]. However, despite the prevalent increase in studies focused on varieties of SCMs and the standardization of the most widely adopted ones such as blast furnace slags and fly ashes, the goals for dependable and widespread cement substitutions have yet to be fully achieved. Apart from confirming the feasibility of SCMs in mitigating the carbon footprint of cement, the sustained growth of interest in both academic and industrial spheres also emphasizes the growing need to continue exploring additional SCMs and their properties. The following discussion sheds light on the current research trends within the domain of SCMs and the questions that remain unanswered.

1.2 Current trends in SCMs

Long before the current global prioritization to reduce dependence on OPC amid mounting concerns about global warming, humanity has been utilizing SCMs. As early as the 10th millennium BCE, and possibly even earlier, human-made calcined lime and finely ground reactive (alumino-)silicate materials, including gypsum cements, were employed. This historical context extends to the development of inorganic binders such as slaked lime, clay, geopolymers, and rammed earth. [16, 17]. In more recent history, technical literature dating to as back as the 1930s have reported the use of blended cements to offset rising energy costs associated with OPC production [18]. Several other scientific studies have reported and promoted the use of SCM substitution of OPC owing to significant enhancement of long-term concrete durability and mechanical strength, along with improvement in binder rheological properties [16, 19–25].

In recent years, the construction industry has widely adopted industrial wastes,

such as blast furnace slags (a byproduct of the pig-iron industry), fly ashes (a byproduct of coal-fired electric plants), and silica fumes (obtained from electric arc furnaces), as primary sources of SCMs. These materials have been extensively researched and commercialized in nearly every country. However, the supply chain for these SCMs is currently under threat in many major concrete-consuming nations due to the increasing awareness and commitment to achieving net-zero targets by 2045, as highlighted by [26]. Furthermore, the global demand for these SCMs far exceeds what industries can currently meet. The worldwide availability of slag, for instance, accounts for only 5-10% of the cement produced, with limited potential for expansion as the demand for steel is not as pronounced as that for concrete. Moreover, iron production and, consequently, slag generation are concentrated in a few countries, further limiting accessibility for major cement consumers. While the quantity of fly ash is greater, its variable quality, with less than one-third suitable for blending in cement, poses challenges[13]. Therefore, it becomes imperative to explore alternatives beyond the commonly utilized SCMs. Despite the extensive study of various SCMs such as rice husk ash or sugar cane bagasse over the last couple of decades, their availability does not currently match the demand.

In this vein, estimations on the availability of varying SCMs and fillers in comparison to the amount of cement produced has shown the vast promise of pozzolans such as calcined clays and volcanic materials as potential future replacements [13, 27]. Clay reserves around the world are 'effectively unlimited' and as such, present substantial prospects of successfully increasing the global amount of SCMs. Clays contain reactive minerals such as kaolinite, smectites, and illites. These minerals have demonstrated pronounced pozzolanic characteristics when activated at temperatures ranging from 700 to 800° C, or subjected to intensive grinding. Activated states of clays are known to exhibit significant potential for interaction with Calcium Hydroxide (CH)[28]. Similarly, natural pozzolans of volcanic origin, cover approximately 124 million hectares of the world's land surface [29]. When combined with lime and water, volcanic materials (VMs) are capable of capturing CH, forming stable compounds with hydraulic cementitious properties [30]. Current research on SCMs is progressively directed towards gaining a thorough understanding and proficiency in utilizing the abundant and promising pozzolans for potential supplementation. Yet, there is much that still needs to be understood, particularly regarding specific physico-chemical characteristics of both material groups, before their practical implementation can be achieved. The subsequent sections offer a concise overview of the latest advancements in the study of clays and volcanic materials, highlighting the areas that require further investigation.

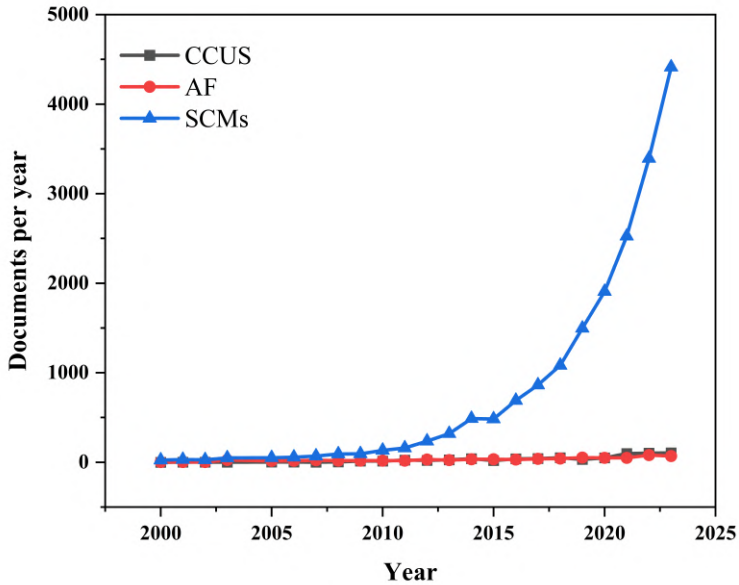


Figure 1.1: Yearly publication of research documents on the topics of carbon capture and storage technologies in the cement sector (CCUS), alternative fuels used in cement production (AF) and supplementary cementitious materials (SCMs). Data has been obtained from the Scopus database.

1.2.1 Clays

From the later part of the 19th century, calcination of kaolinitic clays and the subsequent properties of the metakaolinite formed as a result of it, has been the subject of extensive research [31–38]. Typically, at temperatures of 600-900°C, clay minerals are known to dehydroxylate, leading to partial or complete breakdown of the crystal lattice structure, to form a transitional phase of high pozzolanic reactivity [37]. Upon dehydroxylation, kaolinite undergoes a transformation into metakaolin, characterized by a complex amorphous structure retaining some long-range order due to layer stacking. A significant portion of aluminum in the octahedral layer adopts tetrahedral and pentahedral coordination [28]. Compared to other clay minerals, kaolinite exhibits a substantial temperature gap between de-

hydroxylation and recrystallization, favoring the formation of metakaolin. When the raw clay material is sufficiently pure, metakaolin serves as a highly active SCM, enhancing the compressive and flexural strength, as well as the durability and resistance to chemical attack [37, 39, 40].

However, producing pure metakaolin phases from high-purity kaolinitic clays proves to be three times as expensive as Portland cement [41]. Additionally, the majority of clays worldwide are low-grade kaolinites, containing impurities, and a heterogeneous mineralogical mixture [42]. Notably, low-grade or heterogeneous clays hold the maximum potential, emphasizing that relying solely on conventional metakaolin or kaolin-rich clays as cement replacements is insufficient to fully leverage clays as a resource in cement substitution [43].

As such, recent studies have focused on clays containing low kaolinite contents, upto 40%, combining them with limestone [13, 41, 42, 44–52]. In Limestone Calcined Clay Cements (LC3), aluminates from calcined kaolinite clays react with calcite from limestone and calcium hydroxide from the matrix, producing desirable carbo-aluminate phases. This blend enables the substitution of clinker by up to 45%, offering an attractive low-carbon recipe as a mitigation strategy with low-grade kaolinite clays. these studies have contributed towards pilot scale implementation of low grade clays with a minuimum of 40% kaolinite are abundantly found in sub-tropical regions like India, China, Cuba, and Brazil, where the demand for cement is expected to increase significantly in the coming decades [43, 53]. However, this still does not neccessarily represent the potentials of available clay deposits in the whole world. Of particular interest to the current study, clays found locally in Sweden exhibit lower kaolinite contents, abundance of non kaolinite minerals, and mixed mineralogical characteristics [54–56]. There is a limited number of studies focused on assessment of possible utilization of low or non kaolinite clays.

The recent trend in the field is gradually shifting towards exploring the potential of calcined low-grade clays or those characterized by 2:1 meta-phyllo-silicate structures [43, 57, 58]. However, there remains a significant lack of fundamental understanding regarding these clays, especially those with heterogenous mineralogy. As depicted in Fig 1.2, only approximately 4% of the total studies on pozzolans have investigated the activation and reactive potentials of non-kaolinitic clays, contrasting with the predominant focus on kaolinitic clays. Notably, an even smaller percentage of studies have examined the hydration, pore structure, and long-term performance of non-kaolinitic clays, though this is not explicitly shown in the figure. Comprehensive analyses of activation and reactive potentials are prerequisites for conducting hydration and long-term performance studies on

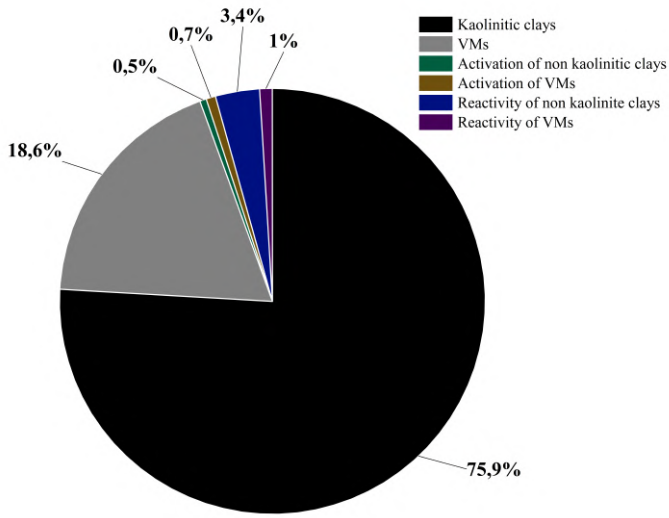


Figure 1.2: The approximate percentage of research papers sourced from the Scopus database, pertaining to various fields of study concerning clays and volcanic materials.As of February 2024, the total number of documents available on research topics related to clay and volcanic materials in concrete is 12,299.

low-reactive heterogeneous clays. As such evaluating these parameters is the first step to comprehensively harness their potentials for use as SCMs.

Furthermore, the activation effects observed in clays utilized for LC3 studies or metakaolin clays may differ for clays with alternative heterogeneous compositions. For example, it is known that certain clay minerals like illites, smectites, mixed layered illite-smectites and sepiolites remain vastly unaffected within 900 °C. For such minerals, mechanochemical activations (MCA), that involve high energy grinding, are known to be more effective as they trigger morphological and physical alterations along with crystal defects. This leads to better amorphization of non kaolinitic minerals [56]. MCA technology has been extensively studied for synthesized or pure-phase clays and single-layered natural clays but lacks comprehensive exploration for potentially low kaolinitic clays [59–62]. The findings from studies on other clays cannot be directly applied to multimineral and mixed-layered clays due to vast differences in mineral compositions, varying impurity levels, and their impact on grindability, specific surface area, and reactivity.

While longer and more intensive grinding regimes in MCA are known to induce extensive amorphization of clays, they can also lead to higher particle agglomeration, influencing reactivity [58]. Optimal grinding duration that is commonly seen to yeild maximum surface areas and minimum agglomerations, is generally reported to be around 20 minutes. This duration is often complemented with specific rpm requirements for different types of clays, based on their compositions [56, 58, 61].

The key to achieving realistic advancements in replacing cement lies in comprehensively understanding the interaction between activation requirements and reactivity potentials of the abundantly available heteregenous clays. Therefore, it is crucial to expand our knowledge in these directions to build our future investigations on.

1.2.2 Volcanic Materials

Volcanic materials have a long and storied history in construction, playing a crucial role in some of the most iconic structures of ancient civilizations. The utilization of volcanic materials, particularly in the form of natural pozzolans, offers a sustainable alternative to OPC. The historical significance of volcanic materials can be traced back to ancient Rome, where they were extensively employed in the construction of monumental structures such as the Colosseum. The Colosseum stands as a testament to the durability and strength of volcanic materials in the form of pozzolanic concrete.

Moving beyond ancient Rome, volcanic materials found popularity in Mayan civilizations in regions of central America and southern Mexico, where volcanic activity is prevalent [63]. The Mayans utilized volcanic glass in their construction practices, showcasing the adaptability and versatility of volcanic materials across different cultures and geographical locations. The ability of volcanic materials to form durable and resilient structures contributed to their widespread use in various architectural endeavors. The popularity of OPC and industrial SCMs has led to a decline in the utilization and research of VMs, despite their widespread availability and untapped potential for construction applications. These volcanic deposits are easily accessible, environmentally friendly, and cost-effective compared to conventional quarrying methods for clay mining.

Contemporary studies emphasize the viability of incorporating volcanic materials as supplements to cement due to their pozzolanic nature, economic advantages, and environmental efficiency [27, 30, 64, 65]. However, the replacement of traditional cement with volcanic ashes is typically limited to around 20% due to observed drawbacks like lower strength, increased vascularity, shrinkage, efflores-

cence, and impaired durability. The primary reason for these limitations is the relatively low reactivity of volcanic ashes compared to other aluminosilicates [66–68].

Similar to clay activations, MCA, has been proposed in several studies for VMs as it helps with modifying physico chemical parameters essential for higher pozzolanic potentials and thereby, aiding an increasing level of future substitution [30, 69–72]. MCA has proven effective in activating low-pozzolanic natural clays but remains insufficiently studied for volcanic materials. Challenges in this regard include a lack of uniformity in milling parameters, such as grinding duration, rpm, ball-to-powder ratio (B/P), and feed size, making it difficult to ascertain suitable parameters for specific classes of volcanic materials. As illustrated in Fig 1.2, less than 2% of papers focusing on pozzolans, encompassing both clays VMs, and only 8% of studies specifically addressing VMs, have discussed the activation or reactivity of VMs. So far, the literature lacks comprehensive information on assessment strategies for both these fundamental aspects, making it challenging to determine which methods are suitable for specific materials. There is inconsistency in evaluating reactivity enhancement in MCA studies, with different tests used and a lack of standardized benchmarks, making comparisons challenging, especially when swiftly screening multiple varieties of VMs. Further research is essential to establish correlations between different milling parameters and their impact on variables affecting the reactivity of specific types of volcanic materials. While R3 and MR3 have been reliably used in recent studies, a comprehensive investigation linking activation associations with VM reactivity levels is notably absent. Moreover, the physical and mineralogical properties of volcanic ashes vary across diverse regions due to factors like source magma composition, diagenetic ages, weathering conditions, morphological traits, and crystal content [72, 73]. This variability necessitates additional studies on the usability of VMs to fully harness their abundant availability and potential as SCMs.

1.3 Research Aims and Questions

Reflecting on the evident gaps explored earlier in understanding and utilization of newer, less-explored yet abundantly available pozzolans like natural clays and volcanic materials has guided the orientation of this thesis. The overarching objective of this endeavor was to develop binders utilizing locally sourced clays and volcanic materials. However, the lack of comprehensive information regarding diverse treatment processes, their impacts on the physical and chemical properties of naturally available pozzolans, reactivity analyses, and mix designs served as

a catalyst for undertaking the current research. The aim is to enhance understanding of the intricate interconnections involved in these processes, specifically in the context of two locally sourced heterogenous natural clays from Sweden and five volcanic materials from Iceland. These materials provide the most accessible options to the Swedish construction market, as SCMs, and hence their treatment or activations are vital for further assessments.

In terms of clays, the research employs a systematic approach, applying thermal activation (TA), mechanochemical activation (MCA), and combinations of both (TA-MCA) treatments to explore the impact of these activation methods on the properties of heterogeneous clays. The focus is on understanding how these activation methods influence crucial parameters such as clay mineralogy, particle size distribution, morphology, specific surface area, and their relation to reactivity. The investigation aims to ascertain whether combinations of thermal and mechanochemical activation can further enhance the modification of these parameters, ultimately achieving higher reactivity for inherently low-reactive pozzolans. The examined clays exhibit mineralogical heterogeneity, including 1:1, 2:1, and interstratified clay phases, along with impurities influencing reactivity. On a similar trajectory to addressing unresolved challenges associated with the utilization of VMs, this study explores the relationship between MCA parameters and the subsequent alterations in properties influencing the reactivity levels.

Subsequent to the understanding gathered about correlations between activation and reactivity, mix designs were formulated to replace varying levels of cement with the activated pozzolans. These mixes were then subjected to hydration to analyze the heat generated during the process, aiming to discern the optimal and effective levels of cement substitution through the correlations of heat evolution.

The following two questions have been formulated to pave the way for further inquiries:

- **Research Question 1**: what are the effects of traditional activation methods on reactivity of natural pozzolans in terms of parameters like chemical amorphization, particle size distributions, and specific surface areas?

- **Research Question 2**: how does the relationship between reactivity and effective substitution level correlate, and is the heat of hydration a sufficient indicator, or is it necessary to rely on long-term measurements of hydration heat or strength to establish this connection?

1.4 Scope of research

The scope of the current research is limited to the following:

1. In terms of activation, the objective of this study is not to devise novel activation treatments but to understand the nuanced correlations influencing the pozzolanic potentials of clays and VMs observed during common reactivity tests like MR3. This understanding was sought in the context of using traditionally employed activation methods. The correlations are absent in existing literature but are crucial for treating relatively newer materials effectively. Specifically, the ball milling parameters employed in the MCA treatements were derived from previous research, which have established optimal thresholds for ball/powder ratio, speed in rpm, and duration.

2. While implementing mechanochemical activations for the pozzolans, the milling duration did not exceed 20 minutes. This decision aligns with insights from various past studies, primarily for two reasons reported in the literature: firstly, prolonged milling beyond 20 minutes at speeds such as 500 rpm is known to induce agglomerations, leading to a subsequent reduction in pozzolan reactivity [56, 58, 72, 74]. Secondly, extended grinding durations can result in elevated temperatures surpassing 200 °C within the ball mill, potentially causing the formation of undesirable phases and introducing handling complications [75]. The selection of 500 rpm as the milling speed was also based on recommendations found in the aforementioned literature.

3. In the investigation of binder reaction kinetics, the current research integrates a pilot-scale study, focusing on only two specific cement replacement percentages as a preliminary study. The aim of this approach is to examine the relationship between the observed reactivity of pozzolans and the 7-day heat of hydration in blended cement pastes. The insights from this stage then serve as a foundation for the potential need for future studies encompassing additional replacement levels, as well as extended assessments of strength and hydrate phases over the long term.

1.5 Thesis outline

The project began with a comprehensive literature review and concurrent preliminary laboratory tests focusing on pre-treatment, activations, characterizations, and reactivity analyses of SCMs. Subsequently, mix designs were formulated based

on observed reactivity levels from tests and mineralogical characterizations. The initial chapter of this thesis contextualizes the research by delving into global trends and the underlying needs driving such investigations, while also outlining the specific research questions targeted in this study. The second chapter offers an overview of the materials utilized for the investigations and the methodologies employed to address the research questions. Moving on, the third chapter presents and discusses the results derived from the investigations, and the fourth chapter concludes the findings while outlining planned future works for the ongoing research focused specifically on hydration studies and durability assessments. This thesis is based on Paper A and Paper B, both of which are attached in Part II of this thesis. The papers that collectively address the initial research question outlined in the study. Throughout relevant sections, these papers are occasionally referenced.

CHAPTER 2

Materials and Methods

This chapter aims to present the material understanding of the pozzolans studied in this thesis. It first presents the geographic origins of the materials, discussing the rationale behind selecting specific locations for material sourcing and highlighting the geological significance that motivate the utilization of these materials. Thereafter the chapter presents the laboratory-scale processing of pozzolans and the methods employed for investigating the properties of the pozzolans linked to activations and eventual reactivity.

2.1 Materials

Two naturally available pozzolans types of heterogneous compositions, have been used for investigations in this thesis - clays and volcanic materials. The following presents the materials in more detail.

2.1.1 Clays

This thesis investigates the objectives through the examination of two distinct, natural clays with heterogenous compositions. The first clay, sourced from the eastern marine region of Norrköping in Östergötland, is a glacial type originally excavated during the construction of the East Link – Sweden's new double track,

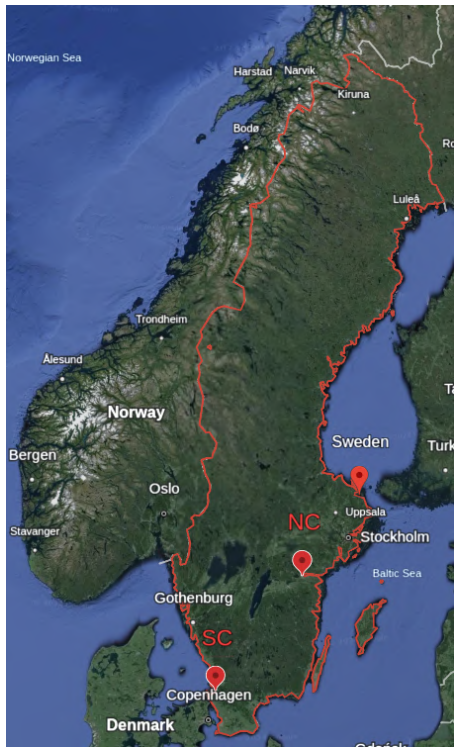


Figure 2.1: Locations where clays were sourced from, in Sweden. NC= Nörrköping clay, SC= Skåne clay.

high-speed railway connection [76]. Previous research on Swedish soils indicates that Östergötland's topsoil has one of the highest clay contents in the country, reaching up to 70%, predominantly composed of clay minerals [77]. The second clay in this study is a sedimentary type from the southern region of Ängelholm in Skåne, with reported mineralogy primarily consisting of kaolinite, substantial amounts of illite, and possible minor amounts of chlorite [78]. The map presented in Fig 2.1 demonstrates the clay locations in Sweden.

The decision to exclusively use clays from these two specific regions is motivated by several factors. Firstly, a preliminary study screening Swedish clays from 15 different regions for potential use as Supplementary Cementitious Materials (SCM) identified the Eastern marine/glacial and Southern sedimentary clays as the most promising in terms of pozzolanic activity, reactivity in a ternary binder

system involving limestone, and strength gain when replacing Ordinary Portland Cement (OPC) up to 30% [79]. Secondly, the prevalence of marine glacial clay in Sweden inspired the choice to study its potential as an SCM. Thirdly, the potential applications of excavated waste clay are understudied locally and globally. Demonstrating the usefulness of a widely available as well as a waste resource for construction, would contribute positively to Sweden's efforts to reduce dependence on cement. Fourthly, unlike several studies on pozzolans that often use industrially processed materials, a lack of processing units that could deliver ready-to-use clays for this study, necessitated manual sourcing from specific locations. This resulted in the identification of limited locations that were accessible for excavation and capable of providing materials with the preferred mineralogy. Norrköping (NC) and Ängelholm (SC) were chosen as the focal locations for this thesis not only because they featured clays with diverse and heterogeneous mineral compositions, which were intended for study, but also because they represented the most readily accessible options for manually sourcing these clays.

The mineralogy of the clays demonstrate heterogenous composition with kaolinite, illite, smectite being the distinguishable clay minerals, along with impurities like quartz and calcite co-existing. The mineral quantification of raw clays through X-ray diffraction (XRD) reveal that NC contains 82% clay minerals while SC has 58%.

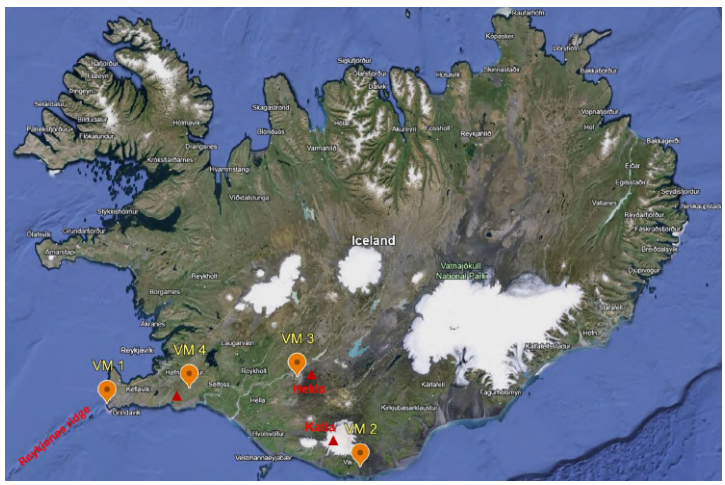


Figure 2.2: Locations of the Volcanic Materials in Iceland

2.1.2 Volcanic Materials (VMs)

The VMs utilized in this thesis were predominantly obtained from four locations in Iceland, specifically sourced from volcanic deposits surrounding Southern regions such as 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. The attached Paper B describes the VMs in more detail.

All the VMs were supplied in their natural, untreated states which necessitated pre-treatments and further activations as detailed in this chapter. Map presented in Fig 2.2 shows the VM locations in Iceland. The VMs used in the study are primarily sourced from the southern part of Iceland, which is more accessible compared to the northern and central regions, where volcanoes are also situated. The volcanic rocks in the southern part of Iceland and are predominantly identified as hyaloclastite, with some having transformed into palagonites [73]. Hyaloclastites are deposits resulting from explosive volcanic activity, formed through the fragmentation of magma either subglacially (under ice cover) or subaqueously (underwater) [80]. They primarily consist of basaltic glass, which is unstable and easily transforms into another volcanic mineral called palagonite, along with secondary minerals. While limited research has been conducted on the pozzolanic properties of hyaloclastites, they are recognized for their siliceous nature and have been identified to possess pozzolanic properties comparable to calcined clays [81].

Recent academic and industrial interest has surged in exploring the extensive potentials of using hyaloclastites. as evident from patent applications and reports [82]. In the current study, except for the deposits sourced from Mt. Hekla, all other volcanic materials are primarily basaltic hyaloclastites with varying levels of silica and alumina. The batch from Mt. Hekla has been identified as pumice, another amorphous high-silica volcanic rock [83]. Pumice has been previously studied and recognized as among the promising SCMs due to its reactivity upon sufficient particle grinding and its ability to contribute to strength gain [68, 83–85]. X-ray diffactograms of the VMs conducted in this study revealed the presence of multiple mineral phases such as albite, anorthite, andesine, oligoclase, cristobalite and quartz - all typically found in volcanic materials [69, 86–90]. The four types of volcanic materials used in the study are representative of a potentially significant resource for substituting cement in the Nordic region.

In addition to the two types of pozzolans, the research incorporated the following materials: Ordinary Portland Cement (OPC 52.5R) from Cementa, limestone (Nordkalk Limus 15), a superplasticizer of PCE type (SP) for clays, supplied by Sika, Switzerland. The superplasticizers employed in the study were specifically designed for the respective clay under investigation, and unfortunately, detailed

product information cannot be disclosed as the product is not yet commercialized. Additionally, for Modified R3 tests assessing pozzolanicity, laboratory-grade Potassium Hydroxide (> 85% purity) and Calcium Hydroxide (>95%) from Sigma-Aldrich were employed. The oxide concentrations of the different materials are provided in Table 2.1.

Table 2.1: 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	12.45	100.07
OPC	19.60	4.50	3.00	63.50	3.50	0.27	2.50	99.53
Limus 15	9.00	0.60	0.30	49.50	-	0.10	-	100

2.2 Methods

2.2.1 Treatment and Activation Methods

Prior to activating, the raw pozzolans were clumpy and saturated with moisture. They were dried at 80°C until constant mass was achieved and then ground for 5 mins in a planetary ball mill (Retsch PM 100), at 200 rpm. The dried clay exhibited a range of sizes, primarily in the form of large hardened chunks. Initially, these chunks were broken down into smaller pieces, each measuring less than 5 mm, using a manual hammer. Subsequently, 60 g of the fragmented material was combined with 30 steel balls, each with a diameter of 15 mm, in a 500 ml ball mill jar, resulting in a ball-to-powder ratio of 8. This process with the noted milling parameters, produced a powdered material capable of passing through a 125 µm sieve. The objective of this step is to ensure the production of finely powdered material for more uniform activation compared to larger fragments. Previous studies have emphasized that pre-grinding prior to activation enhances the homogeneity of pozzolan activation [60, 91].

Following the drying process, the clays were subjected to three specific activation treatments:

1. **Thermal activation (TA) or calcination:** The calcining temperature

for thermal activation of clays was determined through thermogravimetric analysis in a 0-1000°C range under a dynamic N2 atmosphere. Dehydroxylation, observed before 750-800°C, guided the choice of thermal activation at 800°C for 60 mins, aligning with previous studies on similar clays [54, 92]. This duration is optimal for transforming crystalline clay minerals into amorphous states without recrystallization of metakaolin. The activation was performed for 100 g of material in a Nabertherm laboratory furnace, starting from room temperature to 800°C, for 60 mins.

2. **Mechanochemical activation (MCA) without prior calcination:** MCA was performed in a planetary ball mill (Retsch 100PM) for natural Swedish clays, following conditions from [93]. The 500 ml grinding jar contained 12 mm steel balls and uncalcined clay, with a ball-powder (B/P) mass ratio of 25. Milling occurred for 20 mins at 500 rpm, based on observed results in [56, 58]. These studies indicated increased clay particle agglomeration and reduced specific surface areas when grinding exceeded 20 minutes at 500 rpm, with a B/P ratio ranging from 10 to 25.

3. **Combined activations (TA-MCA):** In this treatment, clays thermally activated at 800°C underwent additional MCA to achieve two objectives: amorphization of remaining 2:1 phases and refinement of particle size distribution and specific surface areas for enhanced reactivity. The MCA was conducted for 10 and 20 minutes, while keeping other grinding parameters constant. The resulting clays from combined thermal activation and MCA are labeled TA-MCA10 and TA-MCA20.

For VMs, MCA was conducted in a planetary ball mill at a constant speed of 500 rpm, with a ball-to-powder ratio of 25, consistent with MCA conducted for clays, while varying the grinding duration from 5, 10, 15 and 20 minutes. It was important to avoid speeds exceeding 500 rpm to prevent ball adherence to container walls [75]. Grinding durations were limited to 20 minutes considering insights from prior research on optimal grinding parameters for natural pozzolans and energy consumption considerations [56, 66, 72, 74].

2.2.1.1 Additional notes on challenges related to particle sizes

In the specific context of clays, the treatment and activation steps presented above evolved through a series of initial explorations. The investigation initially centered on thermal activation or calcination of clays, followed by analyses of their pozzolanicity. Various efforts were undertaken to regulate the particle size distribution of both the feed undergoing activation and the calcined material utilized

for subsequent analyses. This initiative stemmed largely from inconsistent flow characteristics observed in both un-calcined and calcined clays. Fig 2.3 demonstrate the inconsistencies observed in flow of uncalcined clays. Flow results from duplicate mixes prepared identically, exhibited variations: some mixes with mixed particle sizes showed minimal to no flow as seen in Fig 2.3 (a), while another sample of the same batch were more flowable. On the other hand, controlled particle sizes in the same water to pozzolan ratio demonstrated improved flow as seen in Fig 2.3 (b). Hence, ensuring repeatability across batches of ground material, necessitated a controlled particle size distribution. Additionally, the link between finer particle sizes and higher reactivities of pozzolans has been well documented [94]. As a first step, prior to calcination, efforts were made to pass the milled

(a) Stiffer mix as observed with mixed clay particle sizes

(b) Improved flows observed with controlled clay particle sizes

Figure 2.3: Effect of mixed and controlled particle sizes on flow properties

material through a 75 µm sieve, to achieve control on the particle sizes. However, production of sufficient material with this specific size range required changes in grinding speeds, longer grinding durations, or a higher B/P, each of which introduced additional complexities such as increased agglomeration, relatively lower yields and possible introduction of structural changes in mineral phases. At this stage, these were undesirable effects as the aim was to solely prepare materials that could be homogeneously calcined.

As such, alternatively, sieving and adjustments to grinding parameters were tested on post-calcinated clays instead of beforehand. However, the issues of ag-

glomeration and low yield persisted and were sometimes even more pronounced. Previous studies have underlined the higher tendencies of calcined clays to flocculate, owing to their higher negative surface charges [95]. Because of agglomerations, clays exhibited lower reactivities than the minimal threshold of the MR3 test, which distinguishes between inert and pozzolanic materials [96]. Furthermore, sieving of milled material was also seen to result in agglomerations, besides proving to be a time-consuming and low-yielding process. Fig 2.4 depict the challenges observed in agglomerations encountered during milling and sieving processes.

(a) Agglomerations after milling calcined clay

(b) Agglomerations of sieved clay

Figure 2.4: Problems encountered while milling and sieving processes

In the next step, as an alternative to grinding, the use of Polycarboxylate Ether (PCE) based superplasticizers was explored to disperse agglomerated particles. To assess the impact of PCE on the dispersion of agglomerated clay particles, calcined clay particles of various size ranges were selected: those passing a 75 µm sieve, those retained on a 75 µm sieve, those retained on a 125 µm sieve, and those retained on a 500 µm sieve. The addition of PCE was found to alter the surface charges of clay agglomerates, particularly aiding in the de-agglomeration of larger size ranges and resulting in higher reactivity (details are available in [97]). Among

all size ranges tested, particles passing through a 75 µm sieve achieved the highest reactivity. However, even this reactivity was below moderate reactivity levels commonly accepted for clays [96]. Additionally, this approach also encountered challenges in mass-producing material for further analyses.

These insights finally led to the development of treatment and activation procedures outlined in section 2.2.1, with particle sieving eliminated after the thermal activation step. Instead, the effects of combined activations through TA and intensive milling through MCA, on the physicochemical parameters of the particles, including particle size, surface areas, and mineral amorphizations, and their influences on reactivity, were investigated. It was noticed that the agglomerations of clays at MCA milling speeds did not result in agglomerations as was previously noticed for lower speeds. It is known that highly intensive grinding at around 500 rpm break structural bonds within clay phylosilicates, essentially aiding in their dehydroxylation. This also leads to alteration of their surface charge effects, facilitating lower agglomerations [98]. As such, associations of combined treatments with modified properties were explored.

2.2.2 Characterization

Mineralogy of the pozzolans were studied by XRD and FTIR. XRD was conducted both before and after activations to detect potential peak shifts upon amorphization. XRD was conducted on BrukerD8 Discover in the 2theta range 5-60°C with step size: 0.02°C, time per step: 0.8 sec. Specific to clays, identification of clay minerals was also conducted on sedimented suspensions and were dried both in air and glycol atmosphere to distinguish swellable minerals like smectites. Additionally. clay minerals were quantified through XRD Rietveld refinement. The test procedures are elaborated in PaperA. The amorphous contents of the activated pozzolans characterized through XRD have been calculated from degree of crystallinity (DOC), presented in Paper B.

The ATR-FTIR spectra of the raw materials were collected on a PerkinElmer Frontier FT-IR spectrometer, in the middle IR (MIR) region, using 2 mg of material. The oxide concentration measurements were conducted on via Inductively coupled plasma atomic emission spectroscopy (ICP-AES). For this method, a prepared sample of 0.1 g is added to lithium metaborate/lithium tetraborate flux, mixed well and fused in a furnace at 1000°C. The resulting melt is then cooled and dissolved in 100 mL of 4% nitric acid/2% hydrochloric acid. This solution is then analysed by ICP-AES and the results are corrected for spectral inter-element interferences. Oxide concentration is calculated from the determined elemental concentration. LOI was measured by TGA where 1 g of the prepared sample is

weighed and placed in an oven at 1000°C for one hour.

For clays, in addition to the above tests, TGA was conducted to also check the dehydroxylation related mass losses in both unactivated and activated states. It was measured by TGA/DSC 3+ Mettler Toledo. Each measurement was performed on clays in an alumina crucible in a nitrogen environment. The clays were heated from 20 °C to 1000 °C with a heating rate of 10 ° /min.

2.2.3 Particle Size Distributions. Specific Surface Area and Morphology

Laser diffraction was conducted using Mastersizer 3000 (Malvern Panalytical) at a rotation rate of 2010 rpm. The dry powders were dispersed in water. The material was added in a beaker until the obscuration was around 10% after which the first measurement was conducted. Thereafter, the beaker was ultrasonicated for 60 seconds to break lumps, after which two consecutive measurements are taken. For specific surface area assessments, BET was conducted on TriStar 3000 with N2 adsorption. The surface morphology of the activated VMs was observed by scanning electron microscopy (SEM) using a FEI Quanta 200 FEG electron microscope.

2.2.4 Reactivity

The effect of activation on reactivity was studied with the modified R3 (MR3) test using an isothermal calorimeter [99]. Various reactivity thresholds have been suggested in literature for these tests, though none has been standardised [100]. Typically, around 100 J/g SCM is used as a predictive range to distinguish inert from reactive SCMs, 200-600 J/g SCM as mid-reactive clays, 150-400 J/g SCM as moderately reactive pozzolans including VMs, beyond 600 J/g SCM as highly reactive clays and beyond 400 J/g SCM as highly reactive VMs [101]. Different thresholds are usually assigned to different categories of pozzolans, based upon variations in anticipated chemical composition and the presence of amorphous or crystalline components [96]. These disparities contribute to varying reaction kinetics over a specified timeframe [81]. This study therefore assumes different reactivity thresholds to categorize reactivity levels of clays and VMs.

Cumulative heat release with the MR3 protocol has reported to offer reasonable prediction of the chemical reactivity of a candidate SCM [99]. The recipe for MR3 involved 1g SCM, 3g CH, in 3.6g of liquid which is 0.5M KOH solution. The mix was stirred for 30 seconds in a vortex mixer (whirli VIB 2. InterMed) and then placed in an isothermal calorimeter (I-Cal Ultra. Calmetrix) at 50 °C, for up to

10 days.

Table 2.2: Mix proportions for different mix types

Type of mix	OPC%	Pozzolan%
Reference (Ref)	100	0
15 Pozzolan	85	15
30 Pozzolan	70	30

2.2.5 Binder designs and Hydration heat

Two kinds of mixes were prepared - a binary set that has pozzolans in 15% and 30% cement replacement levels. Simultaneously, equivalent mixes were prepared, replacing SCMs with fillers using ground norm sand. A constant water-to-binder ratio of 0.5% was maintained for all mixes. The detailed mix designs are provided in Table 2.2. Subsequently, the mixes underwent 60 seconds of stirring for thorough mixing in a vortex mixer and were then placed in an isothermal calorimeter at 20 °C for up to 7 days. The binders incorporating clays were added with PCE superplasticizer in 0.2% by weight of binder, as a former study had demonstrated the higher water demand of the clays [97].

CHAPTER 3

Results and Discussions

The chapter presents the outcomes and analysis of the experiments detailed in the preceding chapter. The results discussed here aim to compare the findings obtained in Paper A relating to clays and Paper B relating to volcanic materials, both of which are presented in Part II of this thesis.

3.1 Mineralogy of activated pozzolans

Fig 3.1 and Fig 3.2 show the effect of activations on the crystal phases of the clays and VMs respectively. The mineralogy of both pozzolans reveal changes in peak intensities and a corresponding modification of the amorphous contents under varying activation treatments. The diffractograms presented in Fig 3.1 reveal notable reductions in peak intensity for both clay and non-clay mineral phases in activated clays. A comparison between thermal activation and mechanochemical activation shows that MCA, particularly when combined with TA (TA-MCA20), leads to more substantial reductions in peak intensity, signifying significant alterations in the clay crystal structure. The observed changes in peak intensities suggest a transformation in crystal structure and subsequent modifications in amorphous contents, as indicated by previous studies [102, 103].

Remarkably, the combination treatment of TA-MCA20 results in the highest

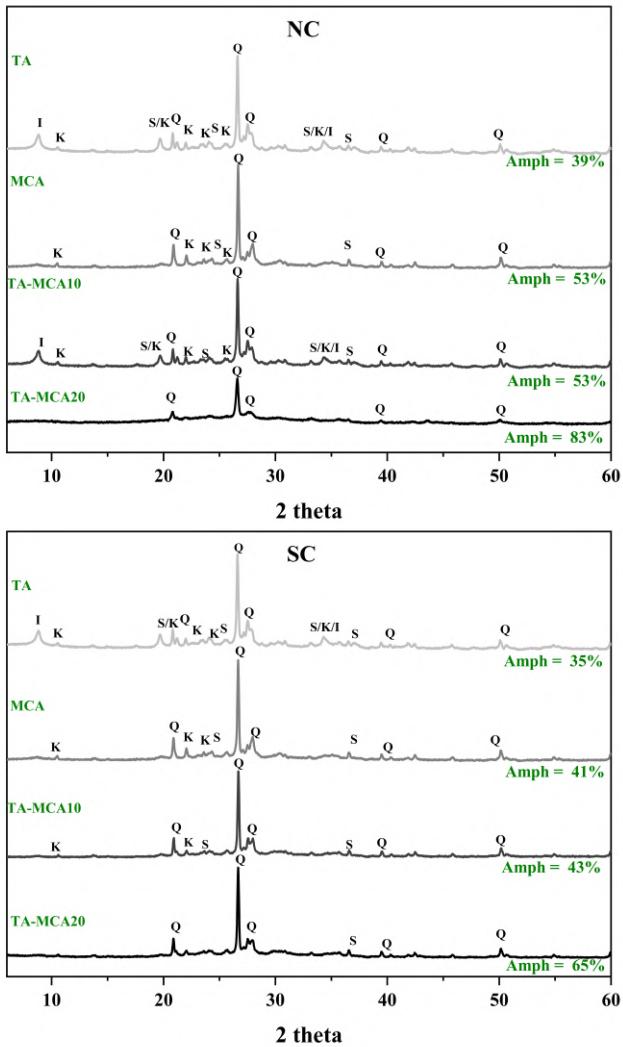


Figure 3.1: The mineral phases and amorphous contents of clays activated under 4 different treatments. S=smectite, I=illite, K=kaolinite, I-S=illte-smectite, C= calcite, and Q= quartz

amorphous contents among all activation methods studied. MCA is known to

induce structural changes in illites and smectites, causing dehydroxylation, which has been reported to be challenging to achieve through thermal activation alone at temperatures below 900 °C [58, 104]. In this investigation, the TA-MCA20 combination treatment yielded the highest amorphous contents. Specifically, in NC the increase was 124% compared to TA and 84% higher than MCA. In SC, the amorphous contents increased by 54% compared to TA and 35% higher compared to MCA under the TA-MCA20 combination treatment. The variations in amorphous contents between the two clays could be attributed to the differing percentages of reactive clay minerals present in each. Notably, SC contains approximately 30% less clay content than NC, contributing to the observed differences in amorphous content levels.

Similar effects were observed in the mineralogy of activated volcanic materials, where increasing MCA durations led to alterations in peak intensities and corresponding modifications of amorphous contents. Unlike clays, in the MCA of VMs, it was noted that at durations typically exceeding 15 minutes, some VMs underwent the formation of new crystal phases. Periclase was consistently identified as one of the phases formed in VM 1, VM 3, and VM 4. In the case of VM 3, the appearance of periclase coincided with a decrease in amorphous content at 15 mins compared to 10 mins of MCA. For other VMs, the emergence of new phases appeared to coincide with peak reductions in other crystal phases, contributing to an overall consistent increase in amorphous contents with prolonged MCA durations.

3.2 Morphology

The effect of activations on the morphology of activated pozzolans are presented in Fig 3.3 which shows the progressive changes noticeable in NC and in Fig 3.4 which shows VM 2. Only one of each pozzolan kind are shown here for discussion. The details of the remaining pozzolans are presented in Papers A and B .

In the context of clays, thermal activation is known to not significantly affect the morphologies which is also seen as the case here [102]. Comparatively, MCA appeared to result in reduced agglomeration and the formation of more rounded and distinct particles. This was also evident in thermally activated clays subjected to at least 10 mins of MCA. Further grinding to 20 mins of MCA on TA clay, led to the production of even more rounded and individual particles with notably less agglomeration.

For VMs, a consistent trend is evident, like in clays, showing that longer MCA grinding durations result in the gradual formation of smaller, fragmented particles

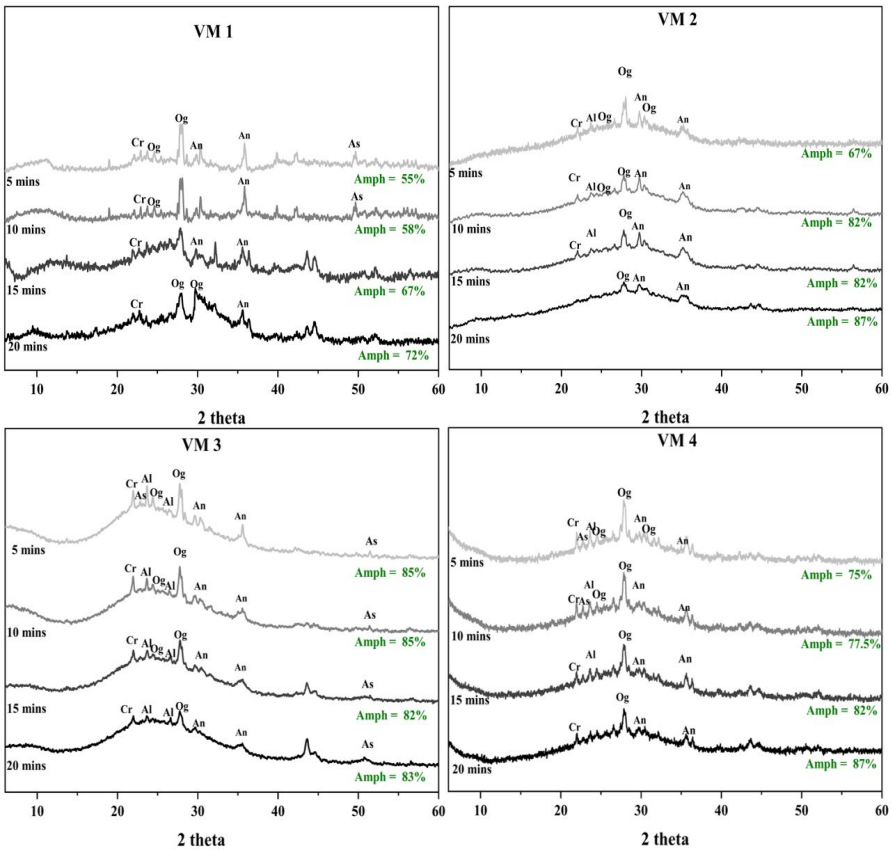
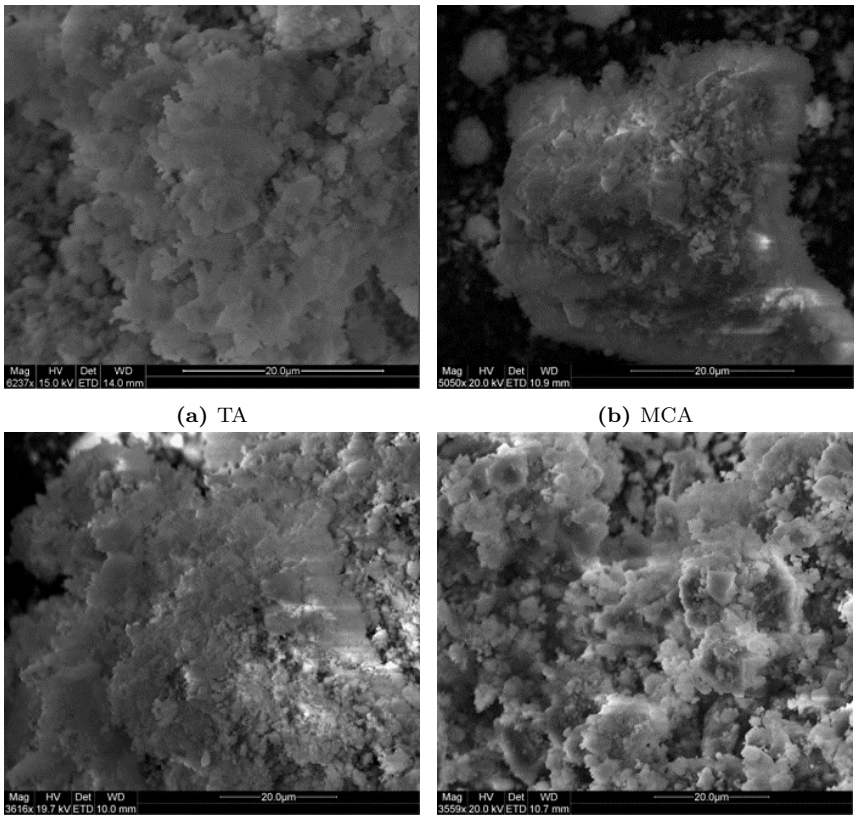


Figure 3.2: The mineral phases and amorphous contents of VMs activated under 4 different MCA durations. An= Anorthite, Cr= Cristobalite, Og= Oligoclase, As=Andesine

across all volcanic materials. Specifically, materials treated for only 10 minutes exhibit distinct fragmentation, particularly noticeable in VMs 2 and 3. As grinding duration increases, there is a noticeable shift toward more spherical particles. VMs 3 and 4 exhibit no discernible further fragmentation beyond 15 mins, where particles from 15 and 20 minutes of grinding appear similar.



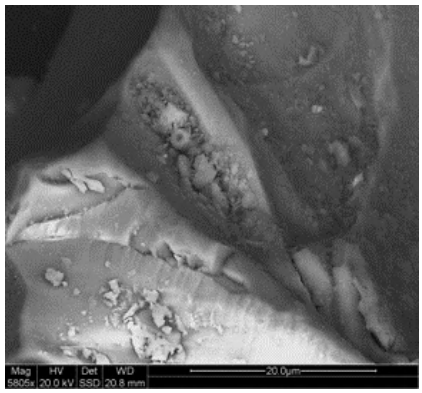
(a) TA **(b)** MCA

(c) TA-MCA10 **(d)** TA-MCA20

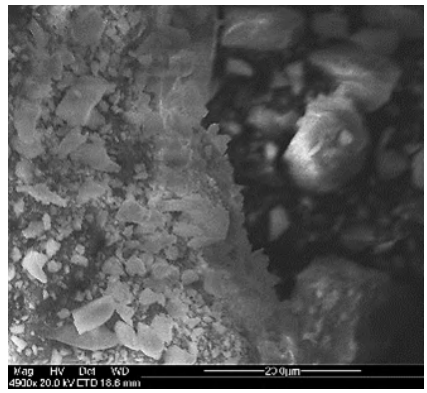
Figure 3.3: Surface morphology of activated NC clay.

3.3 Particle size distributions and specific surface areas

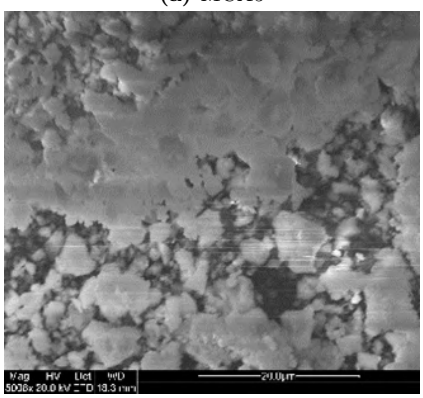
The D50s from particle size distributions and specific surface areas of activated pozzolans are presented in Fig 3.5 (a) for clays and (b) for VMs. In both pozzolans, a consistent trend is observed where lower D50 values correspond to higher specific surface areas measured through BET. In case of clays, this correlation is found to become more pronounced especially under combined activations, such as the TA-MCA20 treatment. In comparison to treatments with MCA alone, the combined



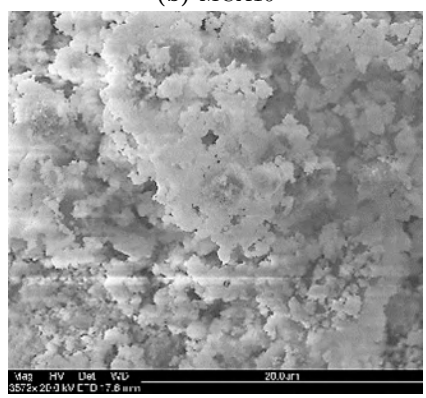
(a) MCA5



(b) MCA10



(c) MCA15



(d) MCA20

Figure 3.4: Surface morphology of VM 2 under the four durations of MCA.

treatments potentially benefit from an additional contribution arising from the preceding thermal activation step. Thermal activation is known to involve sintering and agglomeration due to the heating and cooling processes. Reports indicate that the cooling-induced contraction can mitigate agglomeration tendencies, resulting in a finer particle size distribution for thermally activated clays compared to unactivated ones [58]. Consequently, conducting MCA on a thermally activated clay can lead to higher fragmentation and fracturing than on unactivated clays. Out of the two combinations studied for clay activations, TA-MCA20 was found to have the maximum impact on particle characterisitics.

Between the two clays, the surface areas of NC exhibited greater sensitivity to the conducted activations. Specifically, in NC, the TA-MCA20 treatment resulted in a remarkable 374% increase in surface areas compared to TA and a 158% increase compared to MCA. In contrast, for SC, the combination led to a 95% increase in surface areas compared to TA and an 87% increase compared to MCA. The lower surface areas observed for SC may be attributed to the presence of calcite in it. The reported presence of calcite has been linked to inducing calcium deposition on metakaolin particles during activation, potentially leading to a reduction in specific surface areas [105].

In the case of volcanic materials, the increase of milling durations resulted in progressively higher generation of surface areas. The PSDs presented in Paper B, show sensitivity to grinding durations where in almost all the VMs, PSDs shifted to finer distributions with higher durations. This indicates a potential increase of fragmentation under longer grinding times. However, in case of VM4, the effect of grinding times do not demonstrate stark effect of the particle size distributions. On the other hand, the BET presented in Fig 3.5 (b), shows a remarkable increase in specific surface areas upon prolonged grinding durations for all VMs irrespective of the extent of change in D50 and PSDs. An increase in surface areas may not necessarily be attributed to finer particle sizes; it can also result from altered or fractured morphology, such as the creation of mesopores [106]. Consequently, the PSD might remain similar while more specific surface areas become available for reactions in a morphologically altered sample. This finding is also observed when the results are compared to clays where the MCA and TA-MCA treatments appeared to produce comparable D50s but varying specific surface areas.

In the context of increasing surface areas as a consequence of grinding, VM 4 emerges as notable among the four volcanic materials due to its highest surface areas in all stages. This heightened sensitivity, compared to the other VMs, may be attributed to the inherently greater grindability of VM 4. Grindability is shaped by the geological formations of the materials. Specifically, in the case of hyaloclastites, it is recognized that the hardness of the extracted material can vary based on the type of glacial sedimentation, ranging from loose and easily breakable to nearly rock-solid [107].

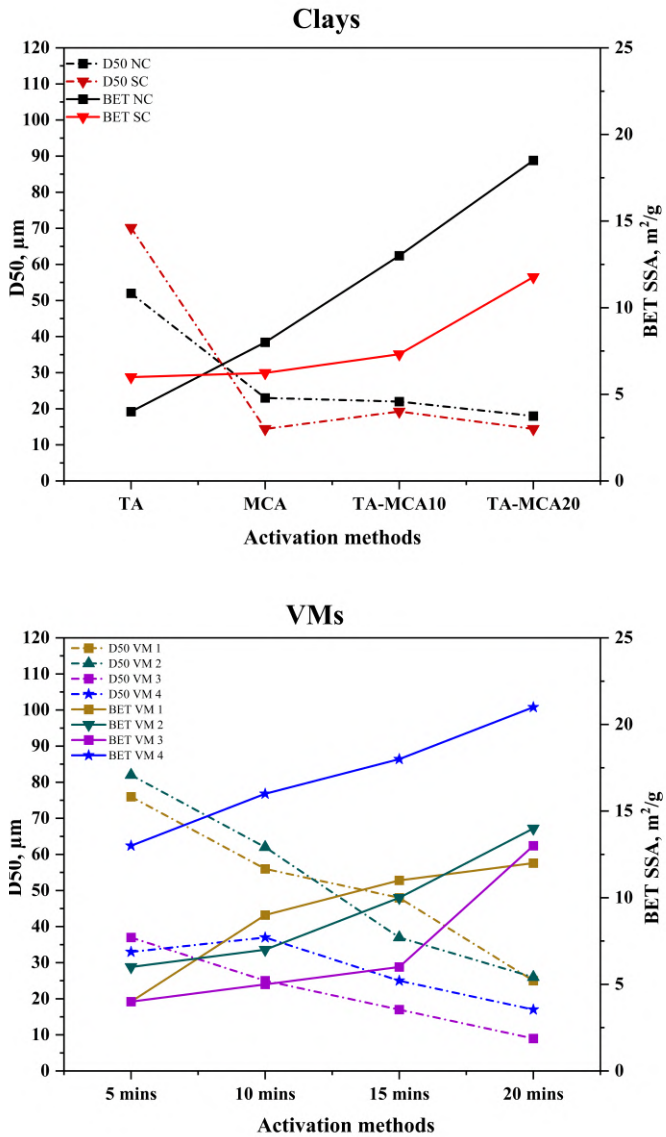


Figure 3.5: Correlation between D50 and Surface areas of the pozzolans

3.4 Reactivity

The reactivity of the activated pozzolans has been investigated as a function of physical modifications brought about by changes in particle sizes and surface areas, and chemical alterations reflected in changes in amorphous contents. In Fig 3.6 for clays and Fig 3.7 for VMs, reactivity results measured through MR3 are depicted, illustrating the correlation between BET and D50 values. The variation in reactive levels is apparent across different activation methods. Additionally, Figure 3.8 illustrates the correlation between the reactivity of all six pozzolans in their most reactive states and their amorphous contents, along with surface areas. This visualization aims to highlight the combined physicochemical effects influencing reactivity.

In the MCA treatment, clays exhibit greater reactivity than TA, as expected due to lower particle size distribution (PSD), higher specific surfaces, and the generation of increased amorphous contents. The higher surface areas provide more reaction sites and enhance the nucleation of reaction products, ultimately accelerating overall reactivity [108]. The combined treatments in clays, particularly TA-MCA20, are associated with the highest reactivity levels compared to all other activation methods, primarily due to the highest modifications in surface areas as seen in Fig 3.6. On the other hand, among the two clays, the variations in reactivity levels achieved upon undergoing the same treatments, are potentially explained by their intrinsic compositions, including factors such as a higher content of reactive clay phases in NC and the presence of impurities like calcite and iron oxide in SC. These impurities may inhibit the dehydroxylation of mineral phases like kaolinite, hindering the achievement of similar reactivity levels as observed in NC. Further details on these discrepancies are discussed in Paper A.

Like the clays, the reactivities of VM appear to be closely correlated with the physical modifications brought about by increasing grinding durations. Notably, the generation of higher surface areas correlate to higher reactivity levels. It is seen that all VMs reached the moderate level reactivity level after 15 mins of MCA. 20 mins induced further increase in reactivities, with VM 4 reaching high level reactivity. Correspondingly, VM 4 exhibited the highest surface area at this stage surpassing all other VMs. Paper B further explores the individual correlations of the VMs.

Fig 3.8 illustrates the comparison of the most reactive states among the six pozzolans resulting from the studied activations. Based on reactivity, two sets of pozzolans with similar reactivities can be distinguished: one set including NC, VM 2, and VM 3, exhibiting MR3 heat levels ranging from 350-355 J/g SCM, and the other set comprising SC and VM 1, demonstrating MR3 levels of 230-233

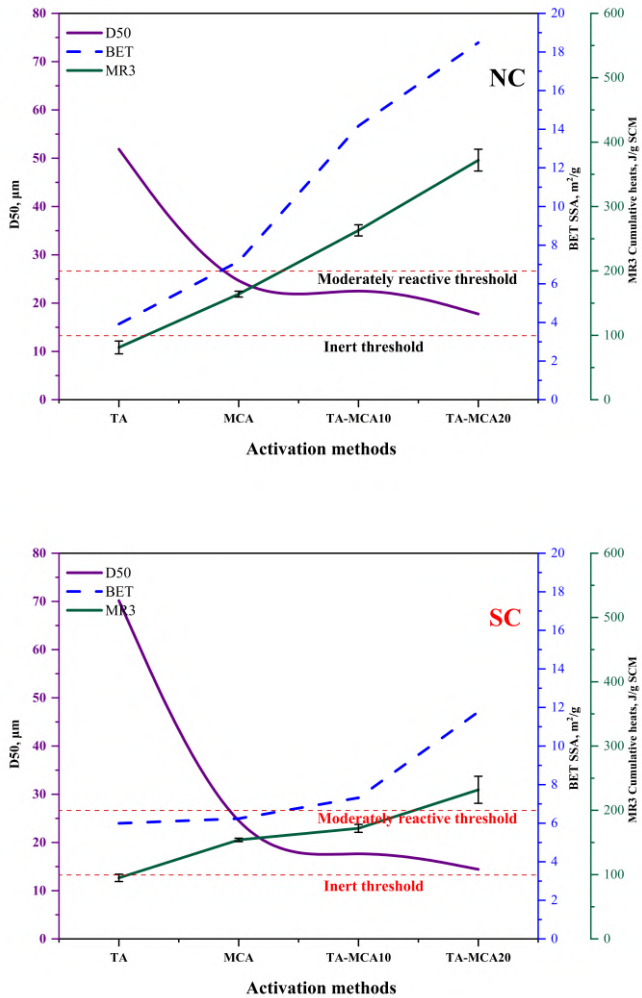


Figure 3.6: Reactivity of NC and SC, in relation to BET specific surface areas and D50. Left hand axis shows D50 values obtained from particle size distributions. Blue right-hand axis shows BET values. Green right-hand axis shows cumulative heat measured via Modified R3 test.

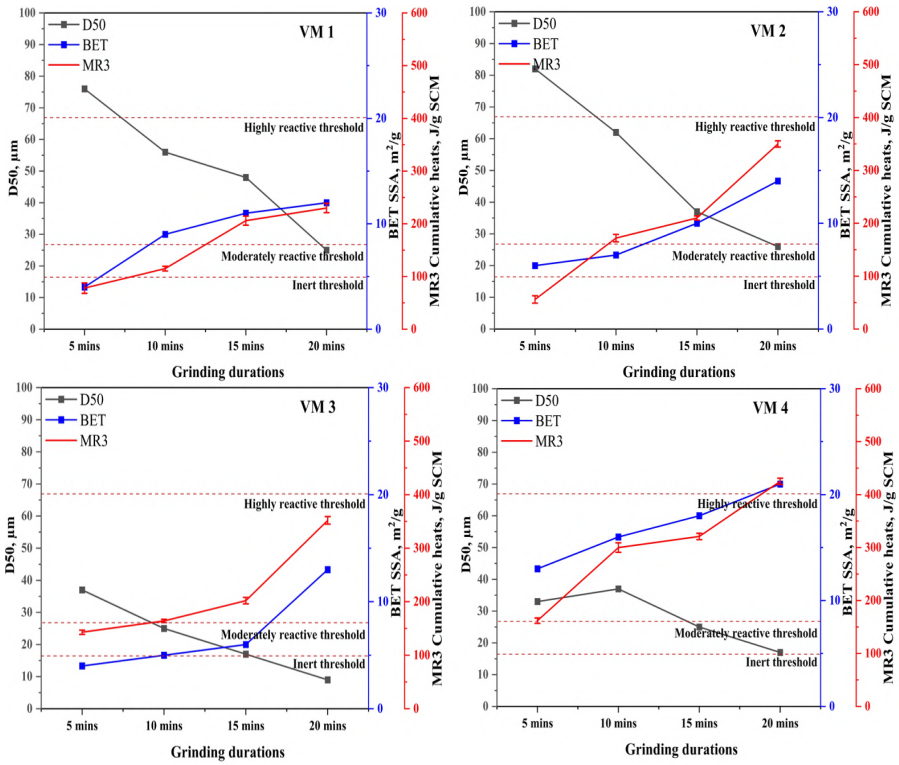


Figure 3.7: Correlations between the MR3 reactivity (red Y- axis), D50 (black Y axis), and the BET specific surface areas (blue Y- axis) of the four VMs activated in the laboratory by milling in four time durations.

J/g SCM. Despite displaying comparable MR3 reactivities within these sets, it is observed that they do not necessarily possess similar particle surface areas or amorphous contents. For example, in the first set, NC exhibits a higher surface area compared to VM 2 and VM 3. However, their amorphous contents reach similar levels under the respective activations, potentially explaining the observed similarities in their reactivities.

Alternatively, within the second comparable set, SC and VM 1 exhibit differing degrees of amorphous content, despite sharing similar surface areas. This variance could stem from variations in reactive silica content among the pozzolans, thus influencing their pozzolanic potentials [14, 109]. This underscores the significance

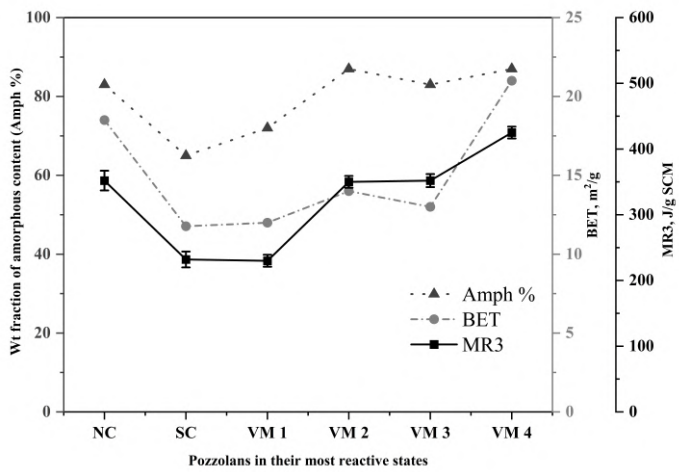


Figure 3.8: Correlation between the reactivity of the six activated pozzolans and their amorphous contents and surface areas at their most reactive states.

of not only considering the levels of amorphous content but also the composition thereof, when evaluating or contrasting pozzolans with diverse compositions. Paper B provides additional insights into the significance of accounting for the presence of reactive silica-based minerals found in volcanic materials, which has emerged as a significant factor contributing to variations in their reactivity levels.

In summary, distinct patterns of correlations are seen to exist among different pozzolans. Reactivity is primarily driven by the physicochemical modifications, particularly amorphous contents and surface areas, induced by various activation methods. However, the chemical composition within the amorphous contents also plays a crucial role in determining how the overall modifications influence pozzolanic activity.

3.5 Reaction kinetics

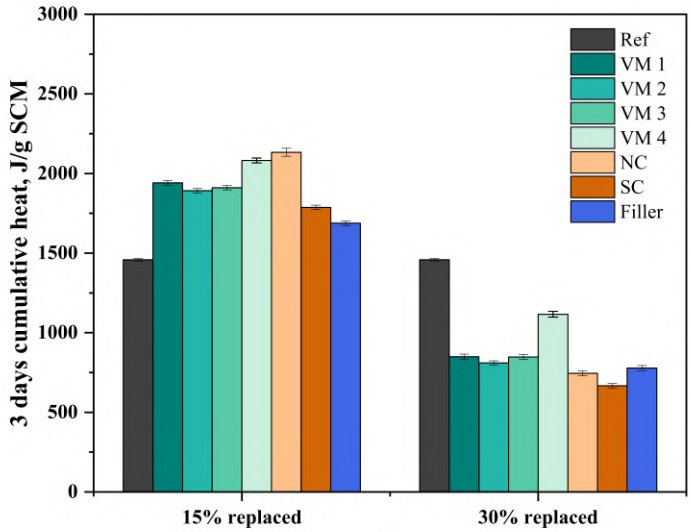
Figure 3.9 illustrates the 3 and 7 days cumulative heat release per gram of SCM, achieved by pozzolanic and filler (quartz) binders at 15% and 30% replacements of OPC. The heat release of the reference with 100% OPC is also provided for com-

parison. It can be observed that at 15% replacements, for all pozzolanic binders, the heat releases surpass those of the reference binder. This phenomenon may be attributed to a combination of three factors: the dilution effect, resulting in more available water per gram of cement particles; higher specific surface areas, creating additional nucleation sites; and the pozzolanic reaction of individual pozzolans [110]. Conversely, the filler binder exhibits heat release equivalent to the reference and lower than that of pozzolan binders. This can be attributed primarily to the dilution and filler effects, as well as the absence of pozzolanic potentials. Overall, it is seen that there are variations among the pozzolans primarily based on their respective differences in amorphous contents and subequent reactivities explored in previous section.

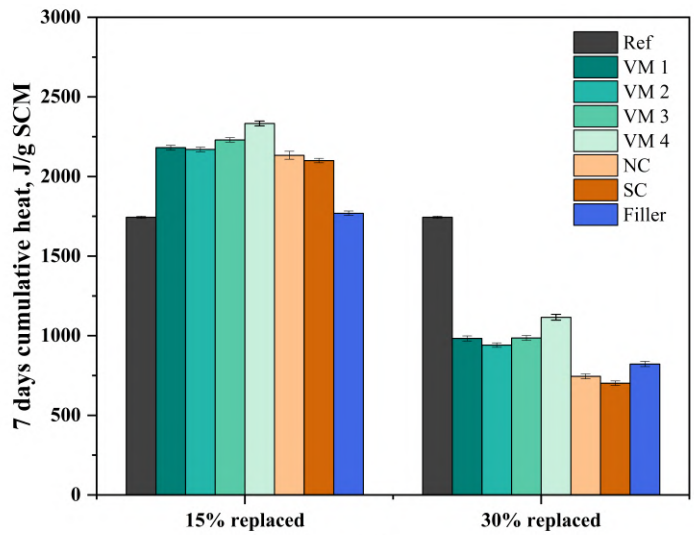
However, at 30% replacements, the blended cement pastes exhibit lower reaction rates and cumulative heat release compared to OPC. This decline could be attributed to the deceleration of the pozzolanic reaction caused by reduced availability of calcium hydroxide (CH) or the inherently slow reactivity of pozzolans. In such cases, extending the 7-day measurement duration may be necessary to assess the pozzolanic potentials over time. However, it is reported that the delayed heat output from slow-reacting pozzolans often necessitates assessments for a duration of approximately 28 days for measurable results [111]. On the other hand,the significant challenge with calorimetry is its reliance on measuring the rate of heat release, which is then aggregated to calculate cumulative heat flow. Over time, the rate of heat release decreases substantially. As a result, even minor inaccuracies in measuring the rate, such as baseline instability or calibration errors, can lead to considerable cumulative errors which could provide a wrong idea about the reaction kinetics [110]. As such, longer calorimetric measurements are not the optimal way to measure slow reacting pozzolans.

Figure 3.10 illustrates the progressive strength development of a single clay sample over a 56-day period. This study, conducted at a pilot scale, focused on assessing the reactivity of a specific pozzolan over time and its impact on strength enhancement. The results indicate a continual increase in strength for both 15% and 30% NC binders with time.

Interestingly, at 7 and 28 days, the strength of the 15% NC binders surpasses that of the reference and fillers, possibly attributed to the filler and dilution effects observed previously (see Fig 3.9). Although the 30% binder exhibits lower strength compared to the others until 28 days, by 56 days, it reaches to the same level of both OPC and the 15% binders. This suggests that substitutions even up to 30% eventually catch up with the strength of the reference material, indicating the potential efficacy of these substitutions in the long term. Moreover, the strength



(a)



(b)

Figure 3.9: Evolution of heat of hydration in 3 days (a) and 7 days (b)

development pattern of NC indicates that the heat releases observed at the end of the 7-day hydration period may not accurately reflect the substitution rates achievable with the use of the activated 6 pozzolans. Based on this preliminary

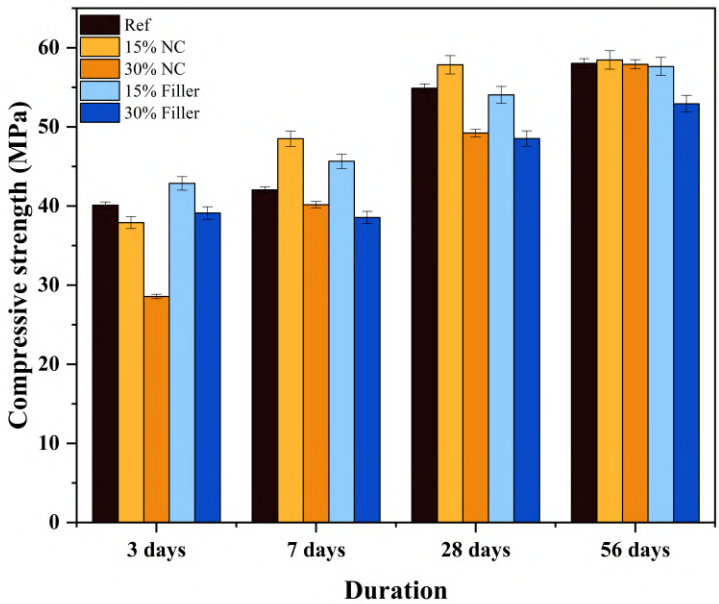


Figure 3.10: Development of strength over time, corresponding to OPC, binary NC and filler binders in 15% and 30% OPC replacements.

insight from a pilot scale analysis towards binder kinetics, further studies can be developed to primarily emphasize mix designing and characterization of hydration at later ages. These studies can then be complemented by investigations into strength development and, over time, evaluations of the pore structure of the pozzolans leading to influences in durability.

CHAPTER 4

Conclusions

This section provides a summary of the research goals and the outcomes of the experimental work conducted to address the posed research questions.

4.1 Conclusions

Partially substituting cement with naturally occurring pozzolans offers a practical solution to address environmental concerns in cement production to some extent. However, till date, several questions have remained unanswered in the context of utilizing widely available, low reactive pozzolans as potential SCMs. In particular, comprehensive understanding of activation and reactive potentials are prerequisites for conducting hydration and long-term performance studies on low-reactive heterogeneous clays.

This study explores the nexus between activation and parameters affecting pozzolanicity of two types of locally sourced pozzolans - clays and volcanic materials. Two heterogeneous natural clays (NC and SC) sourced from Sweden and four volcanic materials (VMs 1-4) sourced from Iceland were examined.

In the investigation, clays initially activated using traditional thermal activation (TA) and mechanochemical activation (MCA) methods exhibited differences in reactivity. Physico-chemical assessments post-activation revealed that MCA,

compared to TA, seemed to amorphize 2:1 clay phases such as illites and mixed-layered illite-smectites, besides also resulting in finer particle size distributions and higher specific surface areas. Nevertheless, despite these improvements, the reactivity remained relatively low for both clays. Combining both the activation treatments, however, produced additional changes in clay mineral amorphization, particle sizes, morphologies, and specific surface areas, leading to higher reactivity compared to uncombined traditional methods.

Similarly, longer durations of MCA for natural volcanic materials affected key parameters, including mineralogy, particle size distributions, morphology, and specific surface areas. These modifications were seen to align with increased reactivities. This correlation provides insights into the activation requirements for volcanic materials in the Nordic region to achieve required levels of reactivity.

The subsequent points summarise the key findings derived from the research:

1. Combined activations of TA-MCA resulted in a significant increase in the specific surface areas of NC clay, with a rise of up to 374% compared to TA alone and 158% compared to MCA. For SC, the respective increases were 95% and 87%. These combined treatments also appeared to concurrently alter the amorphous levels, mineralogy, morphology, and particle sizes of the activated clays, aligning with higher reactivity levels measured through MR3 tests.

2. Among the two clays, the differences in reactivity was potentially brought about by differences in the content of reactive minerals. Specifically, NC, sourced from Nörrköping, containing a higher proportion of reactive clay minerals, was found to be more reactive as measured through the MR3 test. On the other hand, a higher presence of impurities detected in SC, sourced from the region of Skåne, appeared to hinder intrinsic pozzolanicity.

3. Four volcanic materials required a minimum of 15 minutes of MCA at 500 rpm, in a ball mill to achieve moderate level reactivity, as measured through the MR3 test. Milling upto 20 mins produced increased particle fineness, which corresponded to up to 225% higher specific surface areas and a simultaneous average increase in amorphous contents. This aligned with progressive higher reactivity levels of samples produced four grinding durations of 5, 10, 15 and 20 mins. Overall, it was observed that VM 4, sourced from Mt. Litla Sandfell, could achieve high level reactivity after 20 mins MCA, as measured through MR3 test.

4. The differences in reactivities among the VMs was seen to link not only to different levels of surface areas and amorphous contents attained through

grinding, but also to the varying levels of specific reactive minerals constituting the amorphous contents. In particular, higher presence of minerals rich in reactive silica such as cristobalite, oligoclase and andesine, has been found to correlate with higher reactivity. This was particularly seen in the case of VMs such as VM 3 from Mt Hekla and VM 4 from Litla Sandfell.

5. Binder hydration heats of heterogenous pozzolans demonstrate that early measurements of reaction are potentially influenced more by dilution and filler effects than by pozzolanicity. Later age assessments of binder hydrations, complemented with other long term performance based tests are necessary to comprehensively assess evolution of hydration and pore structure of varying substituted blends.

Drawing from the insights from this study, future investigations are planned within the scope of the current PhD. These planned studies are presented in the subsequent chapter.

4.2 Limitations

While this thesis has shed light on intriguing connections between activation treatments and physicochemical changes in less explored pozzolans, a critical reflection reveals areas for further enhancement. By addressing these aspects, complementary studies can be built upon the findings outlined here, paving the way for deeper insights. The following highlights some of the limitations of the current study and potential avenues for complementary researches:

1. **Exploring wider activation parameters:** While the study offers interesting insights into combined treatments for heterogenous clays, it does not seek to provide detailed assessments to determine the optimal combination for specific clay types with distinct compositions. Further research can delve into the complexities of combined treatments, offering invaluable insights for the industrial integration of even low-reactive clays that are abundantly available but underutilized. Similarly, regarding volcanic materials, the study has prioritized a limited commonly used range of grinding parameters. There is therefore a scope to explore the capabilities and parameters of various mills available at both laboratory and industrial scales to expand the understanding of the diverse requirements of different volcanic materials.

2. **Quantified characterizations:** The thesis aimed to gain insight into the overall mineralogy and composition of pozzolans, which undergo modifications through various activation treatments. However, deeper evaluations of mineralogical quantifications were limited, particularly considering the heterogeneous nature of the pozzolans. Nonetheless, it is recognized that such insights (especially of reactive silica amounts) could greatly enhance our understanding of how individual compositions contribute to pozzolanic behaviors.

3. **Comparisons with known SCMs:** To broaden the scope of the analysis on the pozzolans being investigated in this thesis, it would have been valuable to incorporate evaluations of slags and fly ashes which are more established and standardized SCMs. This holistic approach would offer a more comprehensive understanding, particularly relevant from an industrial viewpoint where there's a growing need for alternative SCMs due to their limited availability.

These aspects could motivate further analyses to complement the findings presented in the current thesis. Within the framework of the broader PhD research, the current study has proved instrumental in the understanding required to move to the subsequent phases of the research, using the pozzolans available. The following chapter presents the future studies that have been planned in the following stages of the ongoing PhD work.

CHAPTER 5

Future Scope

This chapter provides the future scope based on the findings established in the thesis.

Future Scope

The thesis establishes crucial correlations to understand the effect of activations on the physicochemical properties of low reactive natural pozzolans, leading to modifications in their pozzolanicities. It was seen that the reactivity of these materials is closely tied to the extent of modifications achievable through activation processes. Conversely, it was also revealed that the impact of modified physicochemical parameters on reactivity may in turn, be influenced by the presence of essential mineral phases in the chemical composition of the pozzolan. Notably, the combined use of MCA and thermal activation methods (TA) significantly improved reactivity for clays. On the other hand, longer durations of MCA application, among the studied time frames, proved advantageous for achieving high reactivity in VMs. A pilot scale study of the contribution of the activated pozzolans to binder reaction kinetics reveal that the pozzolans could be slow reacting and as such, require longer term assessments to understand effective substitution possible with the pozzolans.

The findings from this study raise several research questions that are slated to be explored in the following aspects, during the the upcoming PhD research:

Mix designing

The initial evaluation of pozzolanic binders in two substitute formulations indicates that pozzolans could contribute to reaction kinetics even at a 30% substitution rate over the long term. However, evaluation of this contribution should be complemented by subsequent age-related assessments, such as strength development or pore structure enhancement over time. Additionally, the pilot investigation did not explore the potential benefits of combining limestone with the pozzolans. Combining limestone with aluminosilicates is known to yield carboaluminates, which refine the pore structure and enable greater substitution of OPC. Therefore, a more comprehensive examination is needed to explore a variety of possible mix designs incorporating pozzolans as well as fillers. The following two questions are outlined in that regard:

1. What are the effective substitution rates with pozzolans in focus?
2. Would utilization of fillers create a positive impact on evolution of hydrate phase assemblage?

Planned methodology: Creation of mixes with more levels of substitutions to check development of strength until 56 days, combined with calorimetry.

Hydration

In order to evaluate the hydration properties of the optimized mix designs, it is essential to conduct microstructural analysis of the binder matrix. This analysis will provide insights into the development of hydrate phases and pore structures, both of which have the potential to influence the performance of the binders over time. Incorporation of SCMs and fillers are known to refine pore structure thereby modifying transport and ionic diffusivity of agents deleterious to binders. Hence, it is crucial to understand hydrate as well as pore structures of pozzolanic binders. The following questions are formulated:

1. What are the hydrate phase assemblages of the developed binders?
2. What kind of evolution of pore structure is expected in binders under investigation?

Planned methodology: Evaluation of mineralogy through XRD and TGA, and pore structure through BET, MIP, conductivity measurements.

Transport of chlorides

The process of chlorides binding within hydrate phases has been observed in previous studies, to be facilitated with the use of SCMs, contingent upon the evolution of hydrate phases and pore structure. This binding significantly impacts chloride penetration, thereby influencing the onset of corrosion over time. As chloride ingress is one of the most dominant causes of early degradation of concrete reinforcements, exploring the capacity for chloride binding offered by pozzolanic binders holds significance. Within this topic, the following inquiries are earmarked for investigation, aimed at grasping the interplay between binder microstructure and chloride transport:

1. In the concept of chloride transport, which interactions of chlorides with hydrate phase assemblage is expected?
2. How does the pore connectivity affect chloride transport?
3. Is it possible to use conductivity measurements to reflect upon chloride transport?

Planned methodology: Migration tests including binding isotherm measurements, and subsequent characterizations through XRD, TGA and NMR.

Freezing and thawing

Freezing and thawing present another aspect closely connected with the development of pore structure within binders. As the hydration products of emerging green binders differ from those of hydrated Portland cement, the pore structure, and consequently the pore water content, also undergo variation. Water molecules on pore surfaces and condensation within pore spaces are significantly impacted not only by environmental relative humidity but also by the types and concentrations of ions in the pore solution, which ultimately vary depending on the type and chemistry of the binders utilized. Therefore the following is planned to be studied:

1. How does the pore structure get affected through cycles of freezing and thawing?
2. Which methods can be used for such assessments?

Planned methodology: Evaluation of pore structure through BET, MIP.

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