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LOW-CARBON HIGH-PERFORMANCE BLENDED PORTLAND CEMENTS WITH TAILORED COMPATIBILITY OF THE COMPONENTS

Ph.D. THESIS

SUBMITTED TO THE DEPARTMENT OF MATERIALS SCIENCE
AND MECHANICAL ENGINEERING
AND THE GRADUATE SCHOOL OF ENGINEERING AND SCIENCE
OF ABDULLAH GUL UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

By

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Ph.D. thesis titled “Low-Carbon High-Performance Blended Portland Cements with Tailored Compatibility of The Components” has been prepared in accordance with the Thesis Writing Guidelines of the Abdullah Gül University, Graduate School of Engineering & Science.

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ABSTRACT

LOW-CARBON HIGH-PERFORMANCE BLENDED PORTLAND CEMENTS WITH TAILORED COMPATIBILITY OF THE COMPONENTS

Gizem ARGIN

Ph.D. in Materials Science and Mechanical Engineering

Advisor: Prof. Dr. Burak UZAL

December 2025

This thesis aims to develop low-carbon, high-performance blended cements by holistically investigating the multidimensional interactions of Portland cement (PC), supplementary cementitious materials (SCMs), and superplasticizers (SP). A comprehensive dataset consisting of isothermal calorimetry, thermal analysis, and compressive strength data was generated, and different PC types, replacement rates, SCM fineness, water/binder (w/b) ratio, SP type, and dosage were systematically varied. These data were analyzed with regression-based machine learning models to obtain high-accuracy predictions. While linear models performed well for outputs focused on physical parameters such as early-age compressive strength, nonlinear models (especially Gaussian process regression and artificial neural networks) were found to perform significantly better ($R^2 \approx 0.90\text{--}0.97$) and with lower error for complex and high-variance outputs such as hydration kinetics, CH content, and late-age compressive strength. The Multi-Criteria Compatibility Index, developed by normalizing and weighting different criteria, was applied to a synthetic dataset consisting of 1602 mixtures. The results showed that highly compatible systems had low PC-high SCM content, low w/b ratios, and high SP dosages. Furthermore, SCM with low to medium CaO and high $\text{SiO}_2\text{+Al}_2\text{O}_3$ content increased compatibility. In conclusion, machine learning methods modeled the multivariable interactions in superplasticized blended cements with high accuracy, and the developed compatibility index emerged as an innovative and flexible tool for the preliminary design of low-carbon, high-performance mixtures. This approach contributes to an environmentally, economically, and socially sustainable cement industry.

Keywords: Portland Cement, Supplementary Cementitious Materials, Superplasticizer, Machine Learning, Compatibility index

ÖZET

BİLEŞENLERİN ÖZEL UYUMLULUĞUNA SAHİP DÜŞÜK KARBONLU YÜKSEK PERFORMANSLI KATKILI PORTLAND ÇİMENTOLARI

Gizem ARGİN

Malzeme Bilimi ve Makine Mühendisliği Anabilim Dalı Doktora
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Bu tez çalışması, PÇ–ilave bağlayıcı malzemeler–SP bileşenlerinin çok boyutlu etkileşimlerini bütüncül biçimde inceleyerek düşük karbon salınımlı ve yüksek performanslı katkılı çimentoların geliştirilmesini amaçlamaktadır. İzotermal kalorimetri, termal analiz ve basınç dayanımı verilerinden oluşan kapsamlı bir veri seti oluşturulmuş; farklı PÇ türleri, ikame oranları, ilave bağlayıcı malzeme inceliği, su/bağlayıcı oranı, SP tipi ve dozajı sistematik olarak değiştirilmiştir. Bu veriler regresyon tabanlı makine öğrenmesi modelleriyle analiz edilerek yüksek doğrulukta tahminler elde edilmiştir. Erken yaş basınç dayanımı gibi fiziksel parametre ağırlıklı çıktılarda doğrusal modeller başarılı olurken, hidrasyon kinetiği, CH içeriği ve geç yaş basınç dayanımı gibi karmaşık ve yüksek varyanslı çıktılarda doğrusal olmayan modellerin (özellikle Gauss süreç regresyonu ve yapay sinir ağları) çok daha yüksek doğruluk ($R^2 \approx 0.90-0.97$) ve düşük hata ile çalıştığı görülmüştür. Farklı kriterlerin normalize edilip ağırlıklandırılmasıyla geliştirilen Çok Kriterli Uyumluluk İndeksi, 1602 karışımdan oluşan sentetik veri setine uygulanmıştır. Sonuçlar, yüksek uyumluluk gösteren sistemlerin düşük PÇ–yüksek ilave bağlayıcı oranına, düşük w/b oranına ve yüksek SP dozajına sahip olduğunu; ayrıca düşük–orta CaO ve yüksek $SiO_2+Al_2O_3$ içeren ilave bağlayıcı malzemelerin uyumluluğu artırdığını göstermiştir. Sonuç olarak, makine öğrenmesi yöntemleri süperakışkanlaştırılmış katkılı çimentolardaki çok değişkenli etkileşimleri yüksek doğrulukla modellemiş; geliştirilen uyumluluk indeksi ise düşük karbonlu, yüksek performansa sahip karışımların ön tasarımı için kullanılabilecek yenilikçi ve esnek bir araç olarak öne çıkmıştır. Bu yaklaşım, çevresel, ekonomik ve toplumsal açıdan sürdürülebilir bir çimento endüstrisine katkı sağlamaktadır.

Anahtar kelimeler: Portland Çimentosu, İlave Bağlayıcı Malzemeler, Süperakışkanlaştırıcı, Makine Öğrenmesi, Uyumluluk İndeksi.

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LIST OF ABBREVIATIONS

3DPC	3D printable concrete
AI	Artificial Intelligence
AdaBoost	Adaptive Boosting
ANFIS	Adaptive Neuro-Fuzzy Inference System
ANN	Artificial Neural Network
ASR	Alkali-Silica Reaction
BC	Blended Cement
BFS	Blast Furnace Slag
BR	Bagging Regressor
BSE	Backscattered Electron
CC	Calcined Clay
CC1	Calcined Clay 1
CC2	Calcined Clay 2
CCUS	Carbon Capture Usage and Storage
CEMBUREAU	The European Cement Association
CH ₄	Methane
CO ₂	Carbon Dioxide
CSA	Coupled Simulated Annealing
CSI	Cement Sustainability Initiative
DEF	Delayed Ettringite Formation
DFT	Density Functional Theory
DNN	Deep Neural Network
DT	Decision Tree
DTA	Differential Thermal Analysis
ET	Ensembles of Tree
EU	European Union
EU ETS	European Union Emissions Trading System
FA	Fly Ash
FNT	Flexible Neural Tree
GB	Gradient Boost
GEP	Gene Expression Programming

GGBFS	Ground Granulated Blast Furnace Slag
GPR	Gaussian Process Regression
GS	Grid Search
GTB	Gradient Tree Boosting
HTVS	High-Throughput Virtual Screening
ICDD	International Centre for Diffraction Data
IEA	International Energy Agency
KNN	K-Nearest Neighbor
LC3	Limestone Calcined Clay Cement
LHA	Leonardite Humic Acid
LR	Linear Regression
LS	Limestone
LSSVM	Least Square Support Vector Machine
MAE	Mean Absolute Error
MARS	Multivariate Adaptive Regression Splines
MCCI	Multi-Criteria Compatibility Index
MD	Molecular Dynamics
ML	Machine Learning
NP	Natural Pozzolan
NPA	Natural Pozzolan Association
NZ	Natural Zeolite
OPC	Ordinary Portland Cement
PC	Portland cement
PCE	Polycarboxylate Ether
PMS	Poly-Melamine Sulfonate
PNS	Poly-Naphthalene Sulfonate
PSO	Particle Swarm Optimization
R^2	Coefficient of Determination
RF	Random Forest
RMSE	Root Mean Square Error
RS	Random Search
RT	Regression Tree
SCC	Self-Compacting Concrete

SCM	Supplementary cementitious materials
SDS	Sustainable Development Scenario
SEM	Scanning Electron Microscopy
SF	Silica Fume
SO ₃	Sulfur Trioxide
SP	Superplasticizer
SVM	Support Vector Machine
SVR	Support Vector Regression
TGA	Thermogravimetric Analysis
TPD	Total Particle Density
UNEP-SBCI	United Nations Environment Program Sustainable Building and Climate Initiative
w/b	Water-to-Binder Ratio
w/c	Water-to-Cement Ratio
w/s	Water-to-Solid Ratio
XGB	Extreme Gradient Boost
XRD	X-Ray Diffraction

CEMENT CHEMISTRY ABBREVIATIONS

C ₃ A	Tricalcium aluminate
C ₂ S	Dicalcium Silicate/Belite
C ₃ S	Tricalcium Silicate/Alite
CaCO ₃	Limestone
CH	Calcium Hydroxide
C-(A)-S-H	Calcium-Alumino-Silicate-Hydrate
C-S-H	Calcium Silicate Hydrate



To my family

Chapter 1

Introduction

1.1 Background

Portland cement (PC) is a low-cost and strength-efficient binding material used in structural concrete applications, which makes it the most commonly used binder in the construction industry. Global cement production, which was 4 billion tons in 2017, reached 4.4 billion tons in 2021. Therefore, higher carbon emissions due to this excess production and use increase environmental concerns [1]. Additionally, cement production is expected to increase by 45% from current levels by 2050 [2]. Approximately 6-8% of carbon dioxide (CO₂) emissions, one of the main greenhouse gases, are caused by PC production. Staying with traditional 20th century technologies in areas associated with high carbon emissions, such as the cement and concrete industry, does not seem possible, considering the severity of the problems caused by climate change [3].

According to the United Nations Environment Program Sustainable Building and Climate Initiative (UNEP-SBCI) report, clinker substitution and concrete mix proportioning are the cement industry's two most efficient carbon reduction techniques [4]. Supplementary cementitious materials (SCMs) have the potential to significantly reduce CO₂ emissions by reducing the clinker and cement ratio without requiring high-cost investments [5]. SCMs have been used successfully in blended cements in recent years to reduce clinker content, energy consumption and carbon emissions. Reducing the clinker factor from 0.65 to 0.60 using SCMs, which are highly effective in reducing carbon emissions, could reduce the current annual CO₂ emissions of the cement industry worldwide by approximately 35% [6]. Considering the impact of SCMs in reducing carbon emissions, they can be seen as a game changer in the cement industry.

The use of SCMs in cementitious systems increases long-term strength and durability, but the slow rate of strength development and relatively lower strength at early

ages are important barriers of SCMs [7-9]. Another important barrier is that SCMs cause adverse effects on rheology and workability due to increased water demand, especially at high substitution levels [10]. Superplasticizers (SPs) are included in the system at this point to change and control the workability and rheology of fresh cementitious systems. SPs which are effective dispersants, are surface-active materials that change the surface charge on cement particles. The fluidity of cement paste is affected by the structure, molecular weight, functional groups, and dosage of superplasticizers. In addition to these SP properties, the chemical and phase composition of the cement, its fineness, alkali, sulfate content, and the presence of SCMs affect the compatibility between cement and superplasticizers [11]. SCMs require more superplasticizers than ordinary Portland cement, which also adversely affects rheology, especially at higher substitution levels [12].

The compatibility between Portland cement, SCM, and superplasticizer becomes very important to compensate for the increase in water demand and decrease in strength that occurs when SCMs are used, especially at high substitution levels. [5]. The incorporation of different SCMs (such as limestone, fly ash, and calcined clay) into cementitious systems can affect the interaction between the superplasticizer and the cement [9]. Evaluating the compatibility of the entire system is quite challenging due to the many factors affecting compatibility and the potential for each to influence the other. At this point, data-driven methods such as artificial intelligence and machine learning come into play as a critical tool. The working principle of machine learning, which creates models that optimize material properties, involves feeding input data to the algorithm. Machine learning algorithms have been used in many studies focused on predicting the properties of cementitious materials [13]. The transition from experience and intuition-based techniques to data-guided approaches is seen as crucial to expedite the rate of innovation in cement and concrete research, engineering, and practice. Data science can address the challenges of efficiently and economically providing society's requirements for concrete infrastructure while also eliminating the need for expensive and time-consuming iterative testing [14]. A new era in civil engineering may be initiated by applying machine learning. New developments in more secure, more effective, and sustainable engineering methods can be achieved by using machine learning (ML) to analyze complex information and generate actionable insights [15].

1.2 Research Motivation

The awareness of the whole world of this issue has been clearly demonstrated with the Paris Agreement, in which targets and policies are determined in the fight against climate change. In accordance with the Paris Agreement established at COP 21 in 2015, 195 countries recognized the necessity of limiting the global temperature rise to 1.5°C by regulating their greenhouse gas emissions. Carbon dioxide (CO₂) and methane (CH₄) are the main anthropogenic greenhouse gases [16]. In addition, the European Green Deal, in which the European Union (EU) sets its roadmap for measures to be taken against climate change, is also very important in this regard. The European Green Deal includes a comprehensive and serious green transformation policy for EU member states and non-EU countries that cooperate and trade with EU countries. The cement sector is one of the key sectors in the EU's green transformation roadmap due to its high carbon emissions. There is increasing pressure to develop more environmentally sustainable cementitious systems with lower carbon footprints and higher durability. So, the cement industry is at a critical turning point in its quest for sustainability. The fact that the cement sector is responsible for approximately 6-8% of the world's CO₂ emissions proves that game-changing solutions are urgently needed. Since the manufacturing of Portland cement requires significantly more energy and produces more greenhouse gases than the manufacture of other concrete components, the driving force in sustainable production of cementitious systems is directly related to clinker or Portland cement [8].

According to the International Energy Agency Roadmap for Low-Carbon Transition in the Cement Industry, four primary methods have been identified to reduce CO₂ emissions in cement production: i) improving energy efficiency, ii) switching from conventional fuels to less carbon-intensive alternative fuels, iii) reducing the clinker/cement ratio, and iv) using emerging and innovative technologies such as carbon capture and utilization. The first and the second of the leading methods to reduce CO₂ emissions are carbon capture and clinker/cement ratio reduction, with a 48% and 37% CO₂ reduction potential, respectively. Since the investment and operating activities of carbon capture, utilization, and storage systems are quite high, this choice is expected to increase the cost of clinker production by 2-3 times. Using SCMs as a clinker substitute may significantly contribute to reducing CO₂ emissions without high-cost investments by reducing the clinker/cement ratio [5].

In recent decades, the cement industry has pursued decarbonization strategies, with the partial replacement of Portland clinker by SCMs being one of the most commonly used methods. Nonetheless, the lack of appropriate SCMs has been seen as the main barrier to accomplishing this solution, rather than the performance reduction resulting from clinker dilution [17]. Many interactions between components (PC-SCM) and parameters affecting compatibility must be considered before the appropriate SCM can be identified and incorporated into cementitious systems. Using SCMs as cement replacement materials can benefit cementitious systems by reducing expansions resulting from alkali-silica reaction (ASR), increasing resistance to sulfate attack, and increasing long-term durability and strength. However, some SCMs in particular (e.g., natural pozzolans) have been shown to negatively affect mix workability due to their high water requirements [10]. Superplasticizers can be employed to tailor and control the fresh characteristics of cementitious systems. The compatibility between the SP admixture selected and the cement utilized is a determining factor in achieving the most significant reduction in the water-cement ratio, the highest workability, and the lowest viscosity and yield stress. Furthermore, it is well known that the water reduction performance of SPs could also be negatively influenced by the presence of SCMs [9].

SCMs and superplasticizers have become indispensable components for the sustainable development of cement and concrete technology. In the current approach to the compatibility between the components of cementitious systems, the compatibility between PC-SCM and PC-SP couples is examined separately [18-20]. The compatibility between superplasticizers and blended cements has been tackled by many researchers [9, 11, 21-25]. However, the published literature lacks studies handling the topic with a holistic approach, including the overall compatibility between the components of superplasticized cementitious systems, e.g., PC, SCM, and SP. Addressing the holistic compatibility of all components will be more effective in reducing carbon emissions as it will increase the usability of SCMs in the cement sector. Because even if any SCM seems to be more compatible with a PC and/or SP in terms of performance, it may not be compatible with another PC and/or SP in the same way. This is one of the most important problems in the widespread use of SCMs as a replacement material for Portland cement, and overcoming this barrier is only possible with a holistic compatibility study. As a result of this study, adopting blended cement with low clinker content and, therefore, low carbon emissions will accelerate on an industrial scale.

The evaluation of the compatibility of cementitious systems with a holistic approach is a challenging task due to the abundance of components (PC-SCM-SP) and the interaction of all components with one another. Machine learning (ML) emerges as an influential tool in tackling this complexity, providing exceptional abilities to evaluate multi-dimensional interactions and accurately anticipate the compatibility of cementitious systems with efficiency. ML and associated fields such as data analytics and artificial intelligence have significantly influenced scientific and engineering disciplines by facilitating accurate predictions of complex system behaviors. These methods rely on recognizing patterns in data to develop a response surface that correlates input with output variables. Nonetheless, using these approaches within the field of cement and concrete presents specific challenges. Inherent to these multi-phase, multi-scale systems that endure a variety of processing stages and include a number of partially understood reactions, the high dimensionality of these materials is a critical factor. Moreover, constraints emerge from the limited quantity of datasets, which cannot be readily augmented by automation due to the complexities of sample preparation and the variability in testing. So far, most research in the field has focused on using machine learning to predict the compressive strength of cement and concrete [14]. Even if strength represents a critical property for the cementitious system, furthering the basic understanding of cementitious materials will only be possible by focusing on more advanced properties such as hydration kinetics and pozzolanic activity.

Although traditional experimental techniques are proficient in examining cement components and their interactions, they frequently inadequately address the complex nature of multi-phase, multi-scale systems. Cementitious systems include various complex variables, including hydration kinetics, pozzolanic activity, and compressive strength, which are challenging to optimize simultaneously. ML tackles this complexity by examining extensive, multidimensional datasets, discovering hidden patterns, and precisely predicting material behavior. It reduces the need for time-consuming and resource-intensive trial-and-error experiments, thus accelerating the research process and enhancing resource efficiency [26]. ML provides a structured way to evaluate relationships that may not be evident through conventional testing, especially when multiple parameters interact in nonlinear or competing ways. This expanded analytical capability allows researchers to gain a clearer picture of how individual variables influence overall system performance. Furthermore, the ability to rapidly assess

numerous scenarios contributes to more informed decision-making during mixture design. As a result, ML complements experimental methods by offering broader insights while still relying on experimentally validated data for grounding and reliability.

In this thesis, the characteristics of interest include hydration kinetics, pozzolanic activity, and compressive strength development. Considering the developments in today's construction sector, evaluating only the compressive strength will be insufficient. Therefore, evaluating different behavior (hydration kinetics and pozzolanic activity) increases the value of this study and allows a more comprehensive understanding of the behavior and performance of the components in various contexts. ML is a tool that excels at relating input variables to critical performance outputs. This ability allows for the rapid identification of ideal combinations that balance sustainability with component performance. ML fosters a deeper understanding of how Portland cement, SCMs, and superplasticizers interact by enabling a more holistic evaluation of interactions. In parallel, a Multi-Criteria Compatibility Index (MCCI) will be developed to facilitate easier and more informed material selection by capturing the overall compatibility between blended cement components, which is essential for improving performance while reducing clinker content. Furthermore, different variables were used in both material (different Portland cement, SCM type, and superplasticizer) and experimental parameters (water/binder ratio, fineness of SCM, SCM replacement level, SP dosage) in order to create as large and diverse a dataset for the different experimental results to be evaluated with the ML technique.

1.3 Research Objectives

Reducing the clinker/cement ratio is an effective approach for reducing CO₂ emissions in the cement industry in the next decades. The successful implementation of this method primarily depends on the compatibility of SCMs and SPs with Portland cement, as these admixtures are critical for producing low-carbon, high-performance blended cement. Developing such blended cements necessitates a comprehensive comprehension of the interactions and synergy among the system's components. This thesis focuses on the complex interactions within blended cement systems utilizing machine learning methodology, such as regression analysis, in order to predict and model the correlations among critical variables.

Machine learning will be employed to forecast compatibility trends, enhance material performance, and reveal concealed patterns in the data, offering a more profound comprehension of the cementitious system's behavior. This study used a significantly larger and more thorough dataset than that found in the existing literature. This comprehensive dataset facilitates the production of more precise and reliable results while also permitting thorough assessments of the performance and compatibility of blended cement. Consequently, it becomes possible to model and forecast the interactions among the constituents of blended cement with enhanced accuracy. Therefore, this study will contribute to accelerating the widespread adoption of low-carbon blended cements within the construction industry. The increased usage of these cements represents a significant step towards reducing CO₂ emissions and provides a critical opportunity to promote sustainable practices in the cement sector.

The main research question of the thesis is “What is the set of holistic criteria governing the compatibility between PC, SCM and SP as the components of low-carbon high-performance blended cements?”

On the other hand, the sub-questions of research can be listed as follows:

- How to provide a useful compatibility tool or an index for developing tailored superplasticized blended cements with minimum clinker content as well as comparable hydration kinetics behavior and strength development to ordinary Portland cements?
- How can machine learning be used as an effective tool to better understand the factors governing holistic compatibility between the components?

The main objective of this thesis is that by better understanding with holistic approach the ternary interaction between PC, SCM and superplasticizers and establishing uncomplicated compatibility parameters with the help of machine learning, high performance blended cements with significantly reduced clinker content and hence low carbon emissions can be developed. In line with this objective, a Multi-Criteria Compatibility Index (MCCI) will also be developed to quantitatively integrate multiple performance parameters into a unified evaluation structure. Moreover, by providing a robust framework for compatibility evaluation, this study aims to not only accelerate the adoption of low-carbon cements but also take the sustainability of the cement sector one step further.

1.4 Organization of Thesis

The thesis is organized into seven chapters.

Chapter 1 describes the background, motivation, and main objectives of the study.

Chapter 2 presents a literature review on the low-carbon transition in the cement industry, the use of SCMs and SPs, PC-SCM-SP compatibility, and the application of machine learning in cement and concrete science.

Chapter 3 describes the materials used in the study and provides an overview of the experimental methods utilized throughout the study.

Chapter 4 presents the computational methodology adopted in this study. It provides an overview of the modeling approach, starting with dataset collection and preprocessing steps such as data splitting and correlation analysis. The development of regression models is then described, including cross-validation, hyperparameter tuning, and feature ranking. Model evaluation metrics used to assess the performance of the predictive models are then described. Additionally, a Multi-Criteria Compatibility Index (MCCI) is introduced as a novel framework for comparative model assessment across multiple evaluation dimensions. The chapter concludes with a summary of the overall computational workflow.

Chapter 5 presents the experimental and computational findings of the study, along with critical evaluations of the observed trends. The chapter begins by analyzing the influence of supplementary cementitious materials (SCMs) and superplasticizers (SPs) on hydration kinetics, CH content, and compressive strength across varying replacement levels, types, and mixture proportions. It then transitions to the machine learning-based performance evaluation, where regression models are assessed using different datasets, including isothermal calorimetry, thermal analysis, and compressive strength data. Model performance, hyperparameter tuning outcomes, and feature importance rankings are discussed in detail. The chapter concludes with the introduction and interpretation of the Multi-Criteria Compatibility Index (MCCI), offering a holistic metric to compare cementitious system performance.

Chapter 6 summarizes the concluding elements of the study and provides a perspective on its broader significance and future prospects. It begins with a summary of

the key findings derived from both experimental and computational investigations. The chapter then discusses the societal relevance of the research in the context of sustainable and low-carbon cement industry. Additionally, particular emphasis is given to the development and application of the Multi-Criteria Compatibility Index (MCCI), which serves as an integrative tool for assessing system performance across multiple dimensions. Finally, future research prospects are outlined to guide the continuation and expansion of this work in subsequent studies.



Chapter 2

Literature Review

2.1 Low-Carbon Transition in the Cement Industry

The increase in global CO₂ emissions is a major factor contributing to climate change, threatening ecosystems. The United Nations Framework Convention on Climate Change and the Paris Agreement seeks to limit the global temperature increase to 2°C. In order to meet these climate goals, countries need to establish and execute Nationally Determined Contributions aimed at reducing emissions. In order to meet the requirements of the 2°C scenario of the Paris Agreement, the cement industry, which significantly affects global CO₂ emissions, needs to reduce emissions by 24% by 2050. Many countries are targeting a 40% reduction in greenhouse gas emissions and carbon neutrality by 2030 and 2050, respectively, through strategies such as the EU Emissions Trading System (EU ETS), carbon taxes and emissions trading systems. The need for concrete, and therefore cement, is increasing in direct proportion to the increasing need for infrastructure and buildings due to the increasing global population and urbanization. Global cement production is expected to increase by 12-13% by 2050 [27].

Ordinary Portland cement (OPC), the conventional type of cement, comprises over 90% Portland cement clinker and is produced from widely available and low-cost raw materials. The production method necessitates the grinding and calcining of a clay and limestone mixture at higher temperatures. Clinker, the intermediate material that resulted, is ground to a fine powder and combined with 3–5% gypsum to produce OPC. Approximately 5-10% of total CO₂ emissions in PC production are attributed to electricity consumption during grinding and other processing stages. An estimated 30-40% of emissions result from the combustion of fossil fuels used to generate the high temperatures required for clinker formation. The largest proportion, accounting for 50-60% of total emissions, arises from the calcination process, wherein limestone (CaCO₃) thermally decomposes into CaO and CO₂. This is the reason why CO₂ emissions from

cement manufacturing are distinct from those generated by the combustion of fossil fuels for energy production. Only improving energy efficiency is inadequate for achieving a significant decrease in emissions. Minimizing the calcination of limestone is crucial, as this process substantially modifies the chemical composition of cementitious materials [5, 28].

Globally, the cement sector is the second-largest industrial CO₂ producer and the third-largest industrial energy consumer. Approximately 77% of the energy-related emissions in the concrete chain production are attributed to cement production (see in Figure 2.1) [29]. The demand for cement and concrete is rising due to the increasing global population, urbanization patterns, and the need for infrastructure development. This has placed additional pressure on industry to take action to reduce the carbon emissions of cement production [5]. According to the International Energy Agency (IEA) Roadmap for Low-Carbon Transition in the Cement Industry, four primary methods have been identified to reduce CO₂ emissions in cement production: i) improving energy efficiency, ii) switching from conventional fuels to less carbon-intensive alternative fuels, iii) reducing the clinker/cement ratio, and iv) using emerging and innovative technologies such as carbon capture usage and storage (CCUS). The first and the second of the leading methods to reduce CO₂ emissions are carbon capture and clinker/cement ratio reduction, with a 48% and 37% CO₂ reduction potential, respectively. Improving energy efficiency leads to 0.26 GtCO₂ or 3% of the total CO₂ emissions reductions expected worldwide by 2050. Moreover, the transition to alternative fuels that are less carbon-intensive than conventional fuels will reduce 0.9 GtCO₂, or 12% of the cumulative CO₂ emissions savings by 2050 [6]. In accordance with the sustainable development scenario (SDS), the IEA predicted that the global CO₂ emissions from cement production will decrease from 2.4 Gt in 2019 to 0.2 Gt in 2070. The clinker-to-cement ratio decrease is expected to result in a 14% reduction in CO₂ emissions, while the avoided demand for cement will reduce emissions by approximately 35%. These actions are already mature and will have a significant impact prior to 2030; over 60% of cumulative CO₂ emissions will be reduced by CCUS by 2070, and CCUS will begin to play a role after 2030 [28, 30].

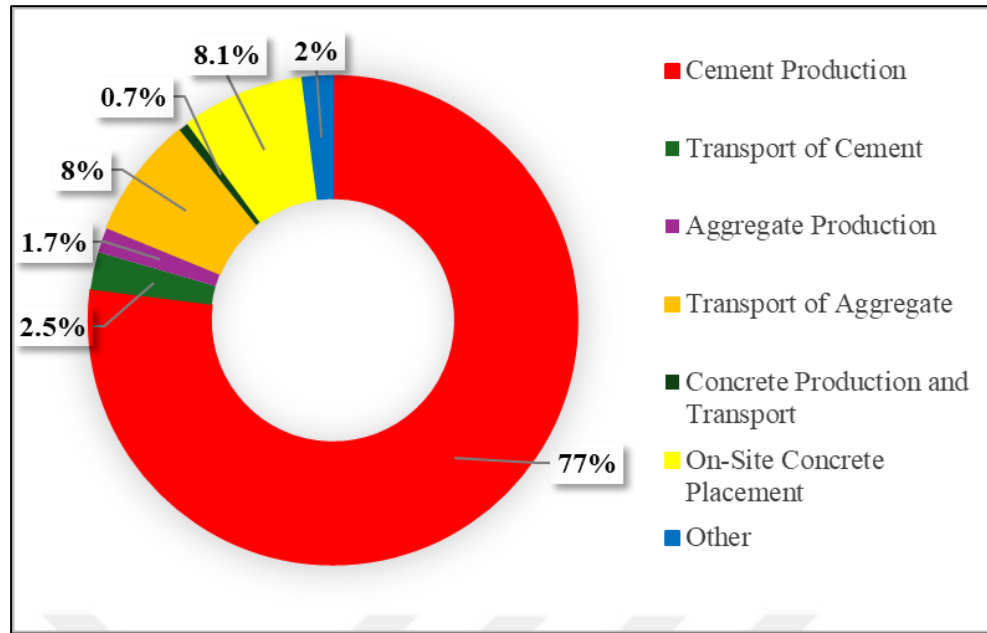


Figure. 2.1 Concrete production chain's energy-related CO₂ emissions (Adapted from [29])

According to the International Energy Agency's (IEA) Breakthrough Agenda Report, total CO₂ emissions from the cement sector in 2024 are higher than in 2015. In addition, the declines observed in the past two years, as represented in Figure 2.2, are attributable to decreases in world production rather than emissions intensity. By 2030, total emissions and emissions intensity will decrease by approximately 20% in the IEA Net Zero Emissions by 2050 Scenario. Therefore, the low-carbon transition for the cement industry is extremely urgent. Key contributors to this goal include increased use of alternative fuels, SCMs improved material efficiency in buildings, and the implementation of CCUS technology [31]. Several obstacles to the implementation of CCUS in the cement industry have been recognized, with the primary challenge being the cost. Using CCUS technology in the cement industry will increase the marginal cost of clinker production by 2-3 times. In addition to the investment cost of CCUS technology, most of the expenses are due to the large amount of energy required to operate the CCUS process. Due to the low profit margin on cement sales, it is exceedingly challenging for the cement industry to incorporate technological components, including CO₂ capture. This would elevate its market price, thereby impeding its competitiveness. The availability of the infrastructure required for CO₂ transport and storage is a second significant challenge to the full-scale deployment of CCUS. Despite the fact that

numerous technological aspects related to transport and storage are technologically advanced, their implementation necessitates political will and public support [5, 32].

Significant initiatives to enhance energy efficiency in the cement industry emerged following the energy crisis of the 1970s [5]. The clinker burning process in cement production demands a significant amount of energy, ranging from 1850 to 2800 MJ per ton of clinker, influenced by variables like the moisture content of raw materials. Using fuel for clinker combustion is responsible for approximately one-third of the total CO₂ emissions produced during the cement manufacturing process. However, efforts to enhance thermal energy demand are limited and incremental, as it is not anticipated that significant efficiency improvements will be achieved. Essential strategies to improve energy efficiency comprise switching coolers, incorporating more cyclone stages, and employing mineralizers to enhance the burnability of raw materials. Precalciner kilns exhibit the highest efficiency and attain the lowest thermal energy requirements. Nonetheless, the capacity for more energy saving is limited by variables such as raw material moisture content and the major investment in capital required to substitute smaller kilns with larger counterparts. Cement manufacturers generally upgrade existing facilities rather than constructing new ones. Moreover, waste heat recovery systems can diminish the total thermal energy required by using heat from preheater exit gases and cooler exhaust air, although they do not directly decrease CO₂ emissions from clinker manufacturing. Although waste heat recovery systems have low conversion efficiency (15-25%) for producing electrical energy, they are profitable in areas with high energy costs and insufficient reliable electricity supplies, such as Japan and China [27].

A retrofit solution that has been extensively studied entails replacing carbon-intensive coal and petroleum coke with cleaner fuel sources. The power sector can phase out coal due to the availability of renewable and clean energy sources. However, the high temperatures necessary for limestone calcination and the critical role of flame temperature in producing high-quality clinkers have historically limited the transition from coal and petroleum coke to cleaner alternative fuels or electricity. However, in recent decades, the transition from a single, wet kiln (i.e., a kiln that dries, dehydrates, calcines, and sinters/burns the raw materials) to a combination of a pre-calciner and a dry kiln (i.e., a kiln that solely performs the sintering/burning process) has resulted in a nearly 50% reduction in the energy required at elevated temperatures and a reduction in the clinker calcination time. This enables the kiln to function at reduced temperatures for an extended

duration, achievable through the use of alternative fuels. In order to reduce CO₂ emissions from cement plants, fuels with lower carbon content, including biomass, natural gas, and municipal solid waste, have been investigated as potential alternatives. Mixtures of biomass-based alternative fuels with coal and petroleum coke are common in industrial applications; by 2050, this mix is predicted to consist of 60% biomass-based fuels, 30% coal, and 10% petroleum coke. The amount of replacement is frequently limited by regulatory requirements and limits, even though some cement plants have investigated alternate fuels with higher replacement fractions [33, 34].

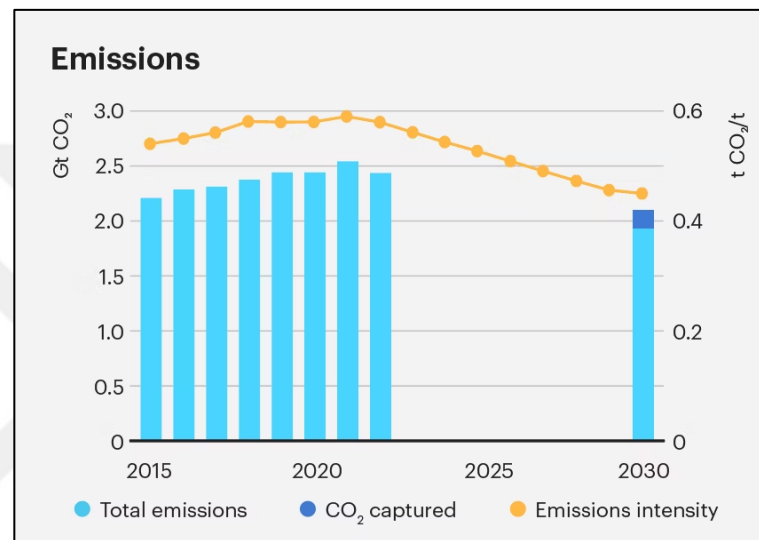


Figure 2.2 Global CO₂ Emissions from Cement Sector (Source: [31])

Currently, the utilization of SCMs has emerged as a critical approach to mitigating CO₂ emissions in cement production. The strategy with the lowest economic and performance impacts on cement and concrete production is using SCMs as partial clinker replacement, which is becoming increasingly apparent. A recent study commissioned by the United Nations Environmental Program Sustainable Building and Climate Initiative (UNEP-SBCI) highlighted clinker substitution and concrete mixture proportioning as the cement industry's most effective low-carbon transition strategies. Alternative techniques may become more viable in an economy subject to carbon taxation [4].

2.2 Supplementary Cementitious Materials: A Key to Clinker Reduction

Supplementary cementitious materials (SCMs) are powders that are soluble siliceous, aluminosiliceous, or calcium aluminosiliceous. SCMs, such as fly ash, ground granulated blast furnace slag, silica fume, calcined clays, and natural pozzolans, are often blended with clinker to produce Portland cement or utilized as a partial substitute for Portland cement in concrete. A significant portion of the materials presently utilized as SCMs are byproducts from other sectors, including fly ash from coal-fired power plants and blast furnace slag from steel production. Some materials are naturally occurring minerals that require significantly less energy for processing than Portland cement production. For instance, the thermal energy intensity of Portland cement clinker is measured at 3.5 GJ/GJ/t clinker. The thermal energy input for fly ash production may be justifiably assigned to power generation rather than the fly ash byproduct. The process of calcining kaolinite clay to produce metakaolin SCM requires a thermal energy input of 0.35 GJ/t clay, which is just 10% of the energy needed for Portland cement clinker. The energy required for producing uncalcined natural pozzolans, like pumice, is significantly reduced. Consequently, utilizing SCMs substantially decreases energy consumption and greenhouse gas emissions associated with cement production, as demonstrated by life cycle analyses [4, 8, 35].

In recent decades, the cement industry has pursued decarbonization strategies, with the partial replacement of Portland clinker by SCMs being one of the most commonly used, practical, and straightforward solutions [17]. The European Cement Association's (CEMBUREAU) 2050 Carbon Neutrality Roadmap report from 2017 indicates that the clinker-to-cement ratio in Europe was 77%. In other words, on average, 23% of clinker was replaced with SCMs, including granulated slag from steel production blast furnaces and fly ash from coal-fired power plants. According to the report, the cement industry recognizes that eliminating coal-fired power plants will restrict the availability of fly ash (10% of total replacements) and reduce slag utilization from the steel sector (33% of total replacements). However, 21% of the overall substitutes comprise natural pozzolans, limestone, or burnt oil shale, while non-traditional substitutes, including calcined clay and silica, are under evaluation. CEMBUREAU's goal is to reduce the clinker ratio in cement from an average of 77% to 74% by 2030 and 65% by 2050 [36].

The utilization of SCMs in concrete, typically in low proportions (5–20% clinker replacement), is frequently motivated by economic factors and enhancements in concrete's long-term mechanical properties and durability. However, the drive to enhance the percentage of clinkers substituted with SCMs is often influenced by industry pressure to reduce CO₂ emissions from cement production. High-volume clinker replacements frequently lead to diminished performance at early stages, prompting research aimed at balancing sustainability with performance [8]. As the substitution level of SCMs increases, the reduction of concrete CO₂ emissions also increases. Nevertheless, the availability of data for quantitative assessment of the impact of the substitution level of SCMs on CO₂ emissions from the concrete production process is not common. Despite this, it is crucial to design the substitution level of SCMs in accordance with the targeted concrete requirements, including initial slump, 28-day compressive strength, and CO₂ reduction, in order to determine the sustainable concrete mix proportions [37].

The lack of appropriate SCMs has been considered one of the most significant obstacles to implementing this method, rather than decreased performance resulting from clinker dilution. The existence of traditional SCMs is under threat due to various reasons (such as the phasing out of coal-fired power plants for fly ash and, the increasing recycling rate of blast furnace slag for steel production, and the transition to electric and hydrogen-powered processes), which necessitates the investigation of different options for SCMs, which are the most important key to effectively reducing CO₂ emissions [17]. Natural SCMs are seen as potential alternative materials with positive aspects such as availability and cost. In addition, studies have shown that a significant increase in long-term strength and improved durability have been observed as a result of the use of natural SCMs in concrete mixtures [22]. Due to the increasing demand for SCMs owing to increasing environmental concerns and the availability problems of many traditionally used materials, natural SCMs or pozzolans are emerging as a promising alternative. As a proof of all this, the Natural Pozzolan Association (NPA) was established in the United States in 2017 [4]. According to the Cement Sustainability Initiative (CSI) database, approximately 75 Mt of natural pozzolans are used as clinker substitutes per year. Natural pozzolan reactivity is highly variable. In addition, the angular particle shape and internal porosity of certain materials can increase water demand and workability difficulties [5].

The performance and durability of SCMs are also enhanced at higher clinker replacement rates due to their involvement in pozzolanic or latent hydraulic reactions.

Pozzolan materials, which are typically low calcium aluminosilicates, such as siliceous fly ashes or natural and calcined pozzolans, undergo a chemical reaction with calcium hydroxide (CH) and water to produce cementitious hydrates. Once activated, latent hydraulic materials can react with water, for example, by soluble alkali. Most latent hydraulic materials utilized as SCMs with Portland cement still require some calcium hydroxide CH in their reaction, which is often provided by the hydration of the Portland cement. The reactive components in the majority of SCMs are the amorphous phases, and materials that contain substantial quantities of amorphous phases consisting of aluminosilicates are considered to be the most appropriate candidates for SCM. Nonetheless, this does not imply that the material is suitable for use in cement or concrete. It should possess appropriate physical and chemical properties, reactivity, and sufficient supply volumes while minimizing adverse impacts on consistency, hydration, strength development, durability, or environmental compatibility. Moreover, certain materials that meet all criteria may be excluded due to incompatibility with established standards and specifications [17].

2.3 Properties of Blended Cement

2.3.1 Hydration Kinetics

SCMs, especially in Portland cement systems, initially act as inert fillers and direct hydration with physical effects, while in the later process they enter into chemical reactions and affect the overall hydration kinetics of the system. This effect is due to the fact that the additives provide more spaces for nucleation and growth of hydration products due to their different surface properties. In addition, non-reactive SCMs indirectly affect the volume and development of hydration products by changing the water/cement ratio of the mixture. The combination of these physical and chemical interactions determines the course of hydration kinetics, especially observed in the first hours, and has a direct effect on the early-age performance of the system. Therefore, it is critical to examine the hydration kinetics in cementitious systems containing SCM [38]. Different studies in the literature on the hydration kinetics of natural pozzolan, slag and calcined clays used in this study are given in Table 2.1 and details of the studies are given below.

Table 2.1 Effects of SCMs on hydration kinetics

Study	SCM Type	Variables	Key Findings
Ardoğa et al.	Natural Pozzolan	3%, 11%, 22% replacement level; particle size (0–10 µm, 35–50 µm, >50 µm)	0–10 µm particles highest heat release due to nucleation effect; >35 µm showed reduced heat due to dilution; higher replacement delayed reactions
Islam and Mohr	Zeolite	5%–20% zeolite	C ₃ A peak decreased with increasing zeolite; limited early-age aluminate dissolution; C-A-S-H phase formation confirmed by XRD; lower total heat due to reduced cement content and reactivity
Schöler et al.	Blast furnace slag	50% replacement level	Alite dissolution delayed; hydration rate reduced; C ₃ S peak shifted and weakened; slag altered pore solution chemistry but improved product distribution
Xie et al.	Blast furnace slag	20% replacement level	Extended induction period; lower total heat than OPC, but higher than fly ash; increased activity in main reaction stage
Yoon et al.	Calcined Clay	CC1, CC2, CC3; 20% replacement level	CC2 (highest amorphous content, 71.9%) had highest reactivity; sharp initial peaks (<2 h) indicated rapid dissolution; broader peak (7–12 h) indicated C-A-S-H/AFm formation
Alujas et al.	Calcined Clay	30% replacement level	800°C calcined clay showed highest reactivity; shortened induction, higher early heat flow, highest 28-day heat; pozzolanic reaction promoted long-term C-A-S-H formation
Avet and Scrivener	Calcined Clay (LC3-50 system)	7 types of calcined clay (17–95% kaolinite)	Higher kaolinite content accelerated early hydration; excessive reactivity led to pore refinement and later hydration slow down

Ardoğa et al., evaluated the early-age hydration behaviors of cement paste mixtures prepared by substituting 3%, 11% and 22% natural pozzolan by isothermal calorimetry method. The obtained results showed that especially fine particles in the range of 0–10 micrometers produced the highest heat of hydration. This is because fine pozzolan particles accelerate reactions by creating a nucleation surface for cement hydration products; this effect is defined as "nucleation effect" in literature. However, in larger fractions, especially in 35–50 and >50 micrometer sizes, heat development decreased due to the decrease in the amount of clinker and the "dilution effect" became dominant. In addition, as the substitution rate increased, the hydration slowed down, and the reactions took longer to start. This effect was observed clearly especially in mixtures containing 22% pozzolan. These findings indicate that both the pozzolan ratio and the particle size should be carefully adjusted in controlling the early-age performance of cement [39]. In the study conducted by Islam and Mohr, zeolite replacement ratios were increased from 5% to 20% and all samples were prepared using a water/binder ratio of 0.45. Isothermal calorimeter results revealed significant changes in the character of the early-age hydration kinetics in cementitious systems replaced with clinoptilolite zeolite. Especially, the secondary peak corresponding to C_3A decreased inversely proportional to the zeolite content; this situation was associated with the limited dissolution of aluminate phases in the system at an early age. The inadequate release of aluminum ions in the early period due to the low solubility of the zeolite caused the limitation of the monosulphate conversion reactions after ettringite formation and thus the suppression of the C_3A peak. In addition, the formation of C-A-S-H phase confirmed by XRD analysis indicates that aluminates cannot follow the classical reaction path of C_3A by binding in alternative hydrate phases. This thermochemical behavior shows that zeolite acts not only as an inert filler in cementitious systems but also as an active phase directing the reaction pathways. As the zeolite replacement rate in the mixture increased, the total heat of hydration decreased. This decrease was attributed to both the lower reactivity of zeolite compared to cement and the decrease in the total amount of cement in the system [40].

In Portland cement systems containing slag, the hydration kinetics change significantly, especially at early ages, as the additive affects both the pore solution chemistry and the nucleation processes. Heat flow data obtained by Schöler et al. using isothermal calorimetry show that slag slows down the dissolution of alite (C_3S) in cement systems, thus causing a decrease in the early-age hydration rate. This effect is largely due

to the fact that the slag provides inert surface area added to the cement matrix, but it also rearranges the thermodynamic and kinetic conditions of the hydration reactions by changing the concentrations of Ca^{2+} , SO_4^{2-} and Al^{3+} ions in the pore solution. It has been reported that especially in the case of high aluminum content, alite dissolution is delayed, and thus the heat flow peak occurs later and with lower intensity. However, the surface properties of the slag facilitate the nucleation of the hydration products, contributing to a more homogeneous and dense distribution of the reaction products [38]. In general, partial substitution of slag for Portland cement significantly affects the early-age hydration kinetics. Since the reactivity of slag is initially low, the main peak of the heat flow curve in such mixtures usually appears with a delay and its intensity is lower compared to the reference Portland cement. This behavior is explained by the limited reaction of slag at early ages and its late participation in the hydration process. However, the contribution of slag to the reaction with calcium hydroxide at late ages increases the total heat release and contributes to the continuity of long-term hydration processes [41]. In the study conducted by Xie et al., it was reported that slag causes a delay in the reaction by extending the induction period in the early stages of the hydration; however, an increase in heat flow is observed in the main reaction stage. This situation shows that slag accelerates hydration by increasing its chemical activity in the future due to its high specific surface area. In addition, the total heat of hydration was found to be lower compared to the control sample containing only Portland cement, but higher than the systems containing fly ash. Therefore, although the inclusion of slag in the cement system slows down the early hydration to some extent, it makes a positive contribution in the later period and improves the overall reactivity and heat release profile of the system [42].

According to the results of the isothermal calorimetry study conducted by Yoon et al., calcined clays exhibited higher heat release at an early age than volcanic ashes, ground bottom ashes, and fly ashes. Sharp peaks formed within the first 2 hours revealed that the calcined clay reacted by rapidly dissolving in alkaline solution; while the second broad peak observed between 7 and 12 hours indicated the formation of C-A-S-H and AFm phases. Cumulative heat release for 7 days for three different calcined clays used in the study was measured as 375, 777 and 647 J/g SCM for CC1, CC2 and CC3, respectively. Especially CC2 exhibited high heat flow even on the seventh day, indicating that the reaction continued after this period. These differences are related to the material properties: CC2 has the highest amorphous phase content (71.9%), while CC3 contains

residual crystalline kaolinite; CC1 contains more inert minerals. Moreover, the significantly coarser particle size of CC2 ($d_{50} \approx 27 \mu\text{m}$) supported the long-term heat release despite the late onset of the reaction. All calcined clays exhibited great pozzolanic character, exceeding the 160 J/g threshold determined by RILEM [43]. The heat evolution in cement pastes, with 30% Ordinary Portland Cement (CEM I 52.5R) substituted by calcined clay, was observed at a constant temperature of 30°C over a duration of 28 days to examine the influence of calcined clay on hydration kinetics. The clay used was a low-grade natural clay containing approximately 40% kaolinite and 40% illite/montmorillonite and was calcined at 600, 800 and 925°C for 60 min. The clay calcined at 800°C showed the highest pozzolanic reactivity due to both high structural disorder and suitable specific surface area. In addition, this calcined clay shortened the induction period, showed higher heat flow at early ages and increased cumulative heat release in the long term. The total heat release over 28 days exceeded both the reference OPC system and the inert quartz added control system. This increase confirms the physical (nucleation and filling) effects of calcined clay as well as the presence of pozzolanic reaction that starts at late ages and progresses with calcium hydroxide consumption. The obtained data show that low-grade kaolinitic clay activated at 800°C thermodynamically enhances OPC hydration and promotes the formation of C–A–S–H [44]. Avet and Scrivener studied using binder systems (LC3-50) containing 50% Portland cement, 30% calcined clay and 15% limestone. In the study, seven different calcined clays with varying calcined kaolinite contents (17–95%) had a crucial effect on pozzolanic reactivity and hydration kinetics. In systems with low calcined kaolinite content, an increase in the heat of hydration was observed, especially in the first days, and this was attributed to the acceleration of C_3S hydration by the filler effect. As the calcined kaolinite content increased, the reaction of metakaolinite with portlandite also accelerated, significantly increasing the heat release from aluminate. However, when the calcined kaolinite content exceeded 65%, the rapid formation of reaction products significantly tightened the pore structure at an early age, creating a very fine pore structure with a diameter of approximately 3–5 nm. In order for new hydration products to grow in such narrow pores, the ions in the solution must reach a much higher saturation level. When these conditions are not provided, the hydration of the clinker phases (C_3S and C_3A) slows down significantly from the third day onwards. This shows that while high calcined kaolinite content accelerates the hydration process at an early age, it can have a limiting effect in the later period [45].

2.3.2 Calcium Hydroxide (CH) Content

Calcium hydroxide/portlandite (CH), formed during the hydration of Portland cement, is a fundamental indicator for evaluating the chemical activity of pozzolanic admixtures in cementitious systems. SCMs containing high amounts of amorphous silica and/or alumina react with CH to form secondary hydration products such as C–S–H and C–A–S–H gels, thus both densifying the microstructure and increasing the strength. These reactions can be represented by the following equations: SiO_2 (amorphous) + CH + H_2O → C–S–H, Al_2O_3 (amorphous) + CH + H_2O → C–A–S–H. Thermogravimetric analysis (TGA), which is widely used to determine the pozzolanic reactivity of SCMs, allows quantitative determination of the amount of CH through the mass loss observed in the range of 400–600 °C. CH consumption directly affects not only the chemical transformation of the binder but also the micromechanical performance of the system. It has been shown that CH is not only a hydration product but also an active component that increases the elasticity modulus by interacting with the C–A–S–H gel. In this context, CH consumption is important for determining the reactivity of SCMs, monitoring microstructure development and evaluating matrix performance [46, 47]. In order to evaluate the pozzolanic activity of natural pozzolans, blast furnace slag and calcined clays used in this thesis, $\text{Ca}(\text{OH})_2$ consumption studies conducted in the literature with the TGA (Thermogravimetric Analysis) method are presented below.

Celik et al. investigated the hydration products in systems where Portland cement was partially replaced by natural pozzolan and limestone powder and especially evaluated CH consumption. In the study, 30% and 50% basaltic volcanic ash (natural pozzolan) and 15% limestone powder replacements were applied. According to TGA results, although an increase in CH amount was observed up to 28 days in the cement paste sample containing 30% natural pozzolan, a significant decrease in CH content was determined in 91 days. This decreases revealed that natural pozzolan dissolved in time and reacted with CH and formed secondary hydration products (especially C-S-H and C-A-S-H gels). These findings clearly show that natural pozzolan actively participates in the hydration process, consumes portlandite and thus contributes to the microstructure of the cement matrix [48]. Khan et al. applied TGA to determine the CH content in cement pastes prepared after 91 days of curing and compared the pozzolanic reactivity of different types of volcanic ash (20% cement replacement). The replacement materials used included fine volcanic ash (VA), ultra-fine volcanic ash (VAF) and VA550, VA650 and VA750 heated

at 550°C, 650°C and 750°C, respectively. TGA curves quantitatively revealed the CH content by correlating the mass loss occurring in the range of 400–500°C with the decomposition of portlandite. According to the data obtained, VAF20 sample was the blended cement paste with the lowest mass loss and the highest depletion of portlandite phase; this was attributed to the increased pozzolanic activity due to its high specific surface area and amorphous silica content. In contrast, lower CH consumption was observed in heat-treated VA samples (VA20-550, VA20-650 and VA20-750), indicating that the reactivity was limited due to crystallization resulting from heat treatment, in agreement with XRD analysis. In particular, VA20-750 cement paste exhibited the lowest pozzolanic performance with the highest portlandite content. These results indicate that TGA is a reliable method for the assessment of pozzolanic reactivity via CH consumption and that mechanical refinement of volcanic ash (e.g. VAF) is a much more effective modification method compared to heat treatment for optimum performance [46]. Ghanim et al., in their studies conducted to compare the pozzolanic performance of pumice and fly ash in cementitious systems, designed a total of ten different mixtures in which cement was replaced with pumice, fly ash and their equal proportion mixtures at 15%, 25% and 35%. Blended cement pastes obtained at the end of 90 days of curing were analyzed in the temperature range of 40–800°C with a heating rate of 10°C/min; CH content was calculated based on the mass loss in the range of 400–500°C. The findings showed that the mixture containing pumice, especially 25% replacement level, had the lowest CH content. This situation reveals that pumice effectively consumes CH, which is one of the hydration products, due to its high amorphous SiO₂ content and promotes the formation of secondary C–S–H gel. Thus, TGA data confirmed that pumice exhibited higher pozzolanic reactivity compared to fly ash [49].

Gruyaert et al. investigated the consumption of CH in Portland cement pastes containing blast furnace slag (BFS) by thermogravimetric analysis (TGA) and backscattered electron (BSE) microscopy. TGA results evaluated the CH content over the mass loss range of 400–500 °C and a significant decrease in the CH amount was detected with the increase in the BFS content. This decrease was explained by the latent hydraulic properties of BFS, which enable it to maintain its hydration by reacting with CH. Especially in the mixtures with a slag to binder ratio of 0.85, the CH content decreased to minimum levels, which was confirmed by the visible decrease of the CH phase represented by a light gray tone in the BSE images. The consumption of CH enabled BFS

to react and at the same time promoted the improvement of OPC hydration. The obtained findings show that BFS contribute significantly to the hydration process in cement pastes both through chemical interaction and microstructural transformation [50]. Similarly, Deboucha et al. found that there was a decrease in CH content with an increasing BFS replacement level. This situation is attributed to both the limitation of CH production due to the decrease in cement amount and the consumption of CH by the latent hydraulic activity of BFS at later ages. Especially at 28 and 90 days of age, lower CH amounts were observed in mixtures containing BFS compared to the reference cement paste, confirming the contribution of BFS to hydration processes [51].

Avet and Scrivener evaluated how portlandite/calcium hydroxide (CH) consumption in LC3-50 binder systems changes depending on the calcined kaolinite content. The results revealed that CH is significantly consumed at an early age, especially in systems containing 50.3% and 95.0% calcined kaolinite. This indicates that metakaolinite reacts rapidly with portlandite to form C-A-S-H and AFm phases. However, when the calcined kaolinite content increases above 65%, CH consumption reaches saturation at an early age and further decrease is limited at later ages. This shows that despite the high pozzolanic activity of the system, the reaction potential is restricted by the depletion of CH reserves. Furthermore, the CH consumption trend confirms the 65% calcined kaolinite threshold, which is a critical limit for both the progress of hydration and the determination of the effective reaction range of metakaolinite. In this context, CH consumption is considered not only as an indicator of reactivity, but also as one of the limiting factors on the microstructure development and phase equilibrium of the system [45]. In their study conducted to evaluate the pozzolanic reactivity of calcined clay minerals in cement pastes, Fernandez et al. monitored CH consumption by thermogravimetric analysis (TGA). For this purpose, cement pastes containing 30% kaolinite, illite and montmorillonite were prepared, and different pastes were formed depending on the calcination temperatures (600 °C and 800 °C). The CH amount was calculated from the mass loss in the range of 450–600 °C by TGA at the end of 28 days of curing. The findings revealed that the systems containing calcined kaolinite showed significant CH consumption from early ages and this situation indicated high pozzolanic reactivity. In the pastes with montmorillonite, limited but increasing CH consumption was observed at late ages. On the other hand, the CH content of the illite added systems remained at a similar level with the inert filler and it was determined that they did not

show chemical reaction. The results obtained show that kaolinite provides the highest reactivity in the cement matrix due to its structural properties, montmorillonite shows limited and delayed effects, and illite behaves largely inert [52].

2.3.3 Mechanical and Durability Performance

In blended cement systems, mechanical and durability performance are two basic criteria that determine both the structural safety and long-term service life of concrete. Pozzolanic admixtures—especially amorphous silica-containing admixtures—react with calcium hydroxide formed as a result of the hydration of Portland cement to form C–S–H gel, thus contributing to the formation of a dense matrix with low permeability. These reactions significantly increase the resistance of concrete to external factors such as chloride ion migration, water absorption, freezing-thawing and acid, sulfate attacks. However, since pozzolanic reactions proceed more slowly than cement hydration, early age strength is generally reduced in concretes containing SCMs. This situation can be limited, especially in applications such as early-age molding or early loading. The main parameters affecting the speed of the pozzolanic reaction are the chemical composition and degree of crystallization of the SCMs, particle size, pH level of the pore solution and curing conditions. It is stated in the literature that the dissolution rate of amorphous silica affects the speed of this reaction. Therefore, evaluating the mechanical and durability performance over time and ensuring appropriate curing conditions in cementitious systems containing SCM are critical for performance optimization [53, 54]. In order to investigate the mechanical and durability performances of natural pozzolans, blast furnace slag and calcined clays in cementitious systems, the findings obtained from the relevant studies in the literature are given below.

The performance of natural pozzolans studied by Kasaniya et al. in terms of compressive strength, electrical resistance and chloride permeability is shown in Table 2.2. Among natural pozzolans, lassenite stood out as the most successful additive in terms of concrete performance. Concretes using lassenite achieved values close to the control mixture in 91-day compressive strength and showed significant improvements in terms of electrical resistance and chloride ion permeability. These positive results can be explained by the fact that lassenite improves the microstructure of the concrete and reduces porosity thanks to its fine particle and suitable chemical composition. Concretes containing pumice showed variability in terms of strength depending on the type of

mixture; some approached the control mixture while some remained below it. However, all types of pumice increased the electrical resistance of the concrete over time and improved durability by reducing chloride permeation. This improvement can be attributed to the silica and alumina content of pumice and the refinement of the pore structure of C-S-H gels formed as a result of pozzolanic reactions. On the other hand, perlite-added concretes exhibited poor performance in terms of both compressive strength and durability properties. The main reason for this is the low fineness of perlite, low reactivity potential and limited binder product formation capacity, which limits microstructure improvement and permeability control. As a result, the contribution of natural pozzolans to concrete performance is strongly dependent on factors such as chemical composition, particle size and grinding degree [55].

Table 2.2 Summary of natural pozzolans' mechanical and durability performance

Pozzolan	91-Day Compressive Strength (Concrete)	Electrical Resistivity	Chloride Permeability
Pumice	Moderate (some below, some close control)	Increased, higher than control	Significantly reduced (improved)
Perlite	Low (did not reach control)	Low or similar to control	Similar to or worse than control
Lassenite	High, in some cases exceeding control	High – significant increase than control	Very low – high resistance

In the study conducted by Mousavinezhad et al., the effects of using locally sourced natural pumice on cementitious systems were investigated comprehensively. Performance criteria such as compressive strength, alkali-silica reaction (ASR) expansion, freeze-thaw resistance, chloride ion permeability and surface resistance were evaluated on mixtures with different substitution rates. The results of these tests are summarized in Table 2.3 according to pumice replacement level, and it was observed that significant improvements were achieved especially in durability properties with the increase in the amount of pumice [56].

Table 2.3 Summary of pumice mechanical and durability performance

Test	Replacement level Pumice		
	10%	20%	30%
Early-Age Compressive Strength (7–28 days)	Moderate reduction; insufficient ASR mitigation	Slightly reduced; acceptable for most applications	Lower early strength; longer setting time

90-Day Compressive Strength	High strength (~43–46 MPa)	High strength (~44–46 MPa)	Fully comparable to fly ash (~44–47 MPa)
ASR Expansion	Expansion > 0.2% — not acceptable	Expansion ~0.05% — acceptable	Expansion ~0.02% — very effective
Freeze–Thaw Durability	Not tested due to poor ASR performance	Durability factor >75	Durability factor >75
Chloride Permeability	Not tested	Very low charge passed (~<1000 C)	Very low permeability and high resistivity

Sabet et al. investigated the replacement of Portland cement with 10%, 30% and 50% ground granulated blast furnace slag (GGBFS). Compressive strength was found to be equal to or higher than the control sample at 28 days at all replacement levels; slight increases in strength were determined especially at 30% and 50% replacements. In terms of durability, 50% GGBS provided an 80% reduction in chloride ion penetrability and was classified as “very low permeability” according to ASTM C1202. Electrical resistivity reached 72 kΩ cm at this replacement level, indicating low corrosion risk. Microstructure analysis showed that the average pore diameter decreased significantly with an increasing GGBS replacement level. However, the carbonation rate increased at 30% and 50% level, but this effect was minimized when sufficient curing was applied. As a result, GGBS replacement provided significant benefits in both strength and durability [57]. Bayat et al. have examined the effects of binary and ternary binder systems containing GGBFS and natural zeolite (NZ) as partial replacements for Portland cement on self-compacting concrete (SCC) in terms of fresh concrete properties, compressive strength, durability performance and environmental effects. In SCC mixtures containing 20%, 30% and 40% GGBFS, 7-day compressive strength decreased significantly (between 20–40%) compared to the reference mixture, but significant increases in strength were observed at 180 days. This decrease can be attributed to the dilution effect of cement replacement with SCMs, which is typical for most SCMs, especially at early ages. In addition, it is explained by the slower hydration of GGBFS compared to cement and the delay in the formation of C-S-H gel that provides binder at early ages. However, over time, the pozzolanic reactions of GGBFS increased, which caused more C-S-H gel formation at later ages and improved microstructure. When evaluated in terms of durability, the increasing GGBFS ratio showed a positive effect on

water impermeability; in the 90-day capillary water absorption test, mixtures containing 30% and 40% GGBFS reached the lowest sorptivity. According to the rapid chloride permeation test, the 90-day diffusion coefficient of the mixture containing 40% GGBFS was approximately 47% lower than the control mixture. In addition, the high electrical resistance values observed at later ages indicate that ion mobility decreased and higher resistance was provided against the permeation of chloride ions. These improvements were attributed to both the formation of a denser microstructure by the reaction products of GGBFS filling the voids and the porous structure becoming less continuous. Therefore, the use of high replacement level GGBFS has barriers in mechanical properties in the short term and provides significant benefits in terms of long-term durability [58].

Yaraghi et al. investigated the compressive strength, and some durability properties of concretes were prepared using low-grade calcined clay. The mixtures were prepared by replacing 30% of Portland cement with only calcined clay (binary) or 20% calcined clay + 10% limestone (LC3). Table 2.4 provides a general evaluation of the compressive strength and durability findings obtained in this study. Binary mixtures showed significant improvements in all durability parameters except compressive strength. The decrease in compressive strength is explained by the dilution effect due to the decrease in the amount of cement; this effect becomes more pronounced especially in LC3 mixtures due to the lower calcined clay ratio. Although LC3 mixtures exhibited a similar trend, their effects were relatively more limited due to the lower calcined clay ratio. These differences were associated especially with the pozzolanic activity of calcined clay and its capacity to make the porous structure denser.

Table 2.4 Summary of calcined clay and LC3 system mechanical and durability performance

Test	Binary (Calcined Clay)	Ternary (LC3)
Compressive Strength	Reduced	Significantly reduced
Water Absorption	Reduced	Inaccurate
Capillary Sorptivity	Significantly reduced	Moderately reduced
Water Penetration Depth	Reduced	Moderately reduced
Electrical Resistivity	Enhanced	Moderately enhanced
Chloride Migration Resistance	Significantly improved	Moderately improved

Chloride Diffusion Resistance	Significantly improved	Moderately improved
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Leo et al. evaluated the compressive strength and durability performance of LC3 systems containing calcined clay and limestone. The results of the tests and the main mechanisms affecting these results are summarized in Table 2.5, and descriptive evaluations are given for each performance indicator. In the tests carried out with mixtures containing 45–65% clinker, 25–40% calcined clay and 10–15% limestone. LC3 concretes showed similar or better results than the reference CEM II concrete in terms of 28 and 90-day compressive strength. In the durability tests, LC3 systems were rated as “excellent” with low permeability and high ionic resistance; however, carbonation resistance was weaker than the reference concrete due to the low portlandite content [59].

Table 2.5 Summary of LC3 system mechanical and durability performance

Test	LC3 Performance Summary	Reason / Explanation
Compressive Strength	Comparable or superior to reference mixes at early and later ages	Influenced by clinker %, calcined clay content, SSA, and alkali content of clays
Surface Resistivity	Higher resistivity than references (indicating lower penetrability)	High SSA and low alkali clays improve resistivity; linked to pore structure refinement
Durability Index (OPI, WSI, CCI)	All LC3 mixes achieved 'Excellent' rating	Synergistic effects: filler effect, pozzolanic reaction, reduced porosity
Carbonation Resistance	Lower than reference	Lower CH content and higher porosity (especially with high-alkali, low-SSA clays)
Chloride Diffusion	LC3 showed much lower diffusion coefficients and surface chloride concentrations than references	Refined pore structure and chloride-binding capacity from LC3 hydrates

2.4 The Role of Superplasticizers in Cementitious Systems

The production of durable structures with a diminished environmental impact is facilitated by using superplasticizers, which are essential components of modern concrete. Their molecular structures and physical-chemical interactions with the cement particle surface are the foundation of their working mechanisms [60]. Superplasticizers (SPs) are polymeric dispersants that are utilized in cementitious materials to either decrease yield stress at a constant solids content or to increase the solids content at a constant yield stress. They are indispensable materials for developing concrete that minimizes its environmental impact. For example, they can be employed to enhance the durability of concrete by reducing the amount of water used, which results in a decrease in porosity and, in particular, a decrease in permeability. Additionally, they can be utilized to decrease the clinker content per unit volume of concrete while maintaining a consistent (or low enough) water/clinker ratio to ensure durability. This enables the use of blended cement with a higher level of clinker replacement [61]. SPs play a crucial role in cementitious mixes by enhancing flowability at low water-cement ratios without causing segregation or bleeding, making them essential for high-performance concrete. Their use can significantly reduce water demand (by 6.5–16%) and increase compressive strength (by over 10–15%). However, while SPs improve workability and strength, they can also lead to unintended negative effects, such as rapid loss of workability, setting time inconsistencies, excessive air entrainment, and increased shrinkage risk. One key factor influencing SP compatibility is cement's tricalcium aluminate (C_3A) phase, which has a strong affinity for superplasticizers. The rheological behavior of cementitious mixtures is influenced by the type and dosage of SP, as well as variations in C_3A and sulfur trioxide (SO_3) content. Loss of workability, segregation, and drying shrinkage can result from the improper use of SPs, demonstrating the necessity of careful selection and dosage to optimize performance. Higher C_3A levels can lead to excessive adsorption of superplasticizers, reducing their efficiency and causing loss of workability [19, 62]. The interaction between superplasticizers and cement hydration products is crucial in determining setting time, strength development, and long-term durability [63–65].

Superplasticizers are classified into various families based on their chemical composition and mechanism of action, such as polycarboxylate, lignosulfonate,

naphthalene, and melamine-based types. Lignosulfonate, naphthalene, and melamine-based admixtures function similarly, as both contain sulphonate groups that adsorb to the surface of cement particles, giving an electrical charge (see Figure 2.3 (a)). This charge generates electrostatic repulsion between the particles, effectively dispersing them and releasing previously trapped water. As a result, less water is required in the cementitious mixture. In contrast, one of the most widely used superplasticizers today is polycarboxylate ether (PCE), which features branched side chains. These admixtures consist of a charged backbone that adheres to cement particles. At the same time, the bulky ether side chains promote dispersion and prevent flocculation not only through electrostatic repulsion but also via steric hindrance (see in Figure 2.3 (b)) [66, 67]. Nevertheless, these admixtures are specifically formulated for Ordinary Portland Cement (OPC); consequently, their plasticizing efficiency may be influenced by using SCMs [68].

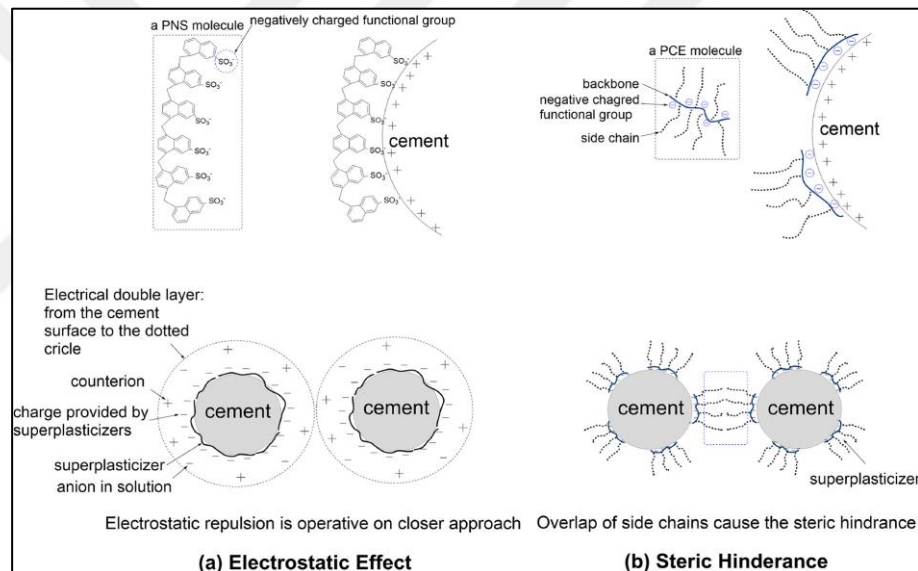


Figure 2.3 Schematic representation of (a) electrostatic repulsion and (b) steric hindrance (Source: [67])

SCMs such as fly ash, slag, silica fume, etc., provide significant environmental and performance advantages by reducing clinker content and enhancing long-term durability [69]. However, blended cements often exhibit reduced workability due to variations in particle size distribution and surface chemistry, necessitating the use of superplasticizers to improve flowability and hydration efficiency [9]. The performance of superplasticizers in blended cement systems is heavily influenced by their compatibility with factors such as the type of SCMs, cement composition, chemical composition of admixtures, particle size, fineness, etc. This compatibility plays a key role in determining the workability of

the fresh state of the cementitious system and the strength and durability of the hardened cementitious material [9, 22].

2.5 Compatibility of PC, SCMs, and SPs in Cementitious Systems

The compatibility between Portland cement (PC), supplementary cementitious materials (SCMs), and superplasticizers (SPs) is a critical factor influencing the fresh and hardened properties of cementitious systems. The interactions among these components affect key parameters such as workability, rheological behavior, setting time, and long-term durability. Variations in the chemical and mineralogical composition of SCMs, coupled with differences in the molecular structure and adsorption characteristics of SPs, can lead to significant changes in cement hydration kinetics and dispersion efficiency. Understanding these interactions is essential for optimizing mix design, ensuring stable performance, and mitigating issues such as early stiffening, segregation, or excessive retardation [70]. Due to the critical importance of component compatibility in cementitious systems, various studies in literature have examined several compatibility aspects, including interactions between PC and SPs, PC and SCMs, and blended cement and SPs. Some studies that reveal the compatibility relationships between cement, SCM and SP are summarized in Table 2.6. This table provides a comparative framework in terms of the types of cement and additives used, types of superplasticizers, experimental methods applied, and the main findings obtained. In general, it is seen that the interaction patterns of different superplasticizers (e.g. polycarboxylate, naphthalene, melamine, lignosulfonate) with different SCMs (silica fume, fly ash, slag, metakaolin, glass powder, etc.) are quite variable and these interactions directly affect performance criteria such as workability, hydration, rheological behavior and strength. Each of the factors such as cement type, SCM type, SP structure and dosage play a decisive role on the compatibility of the system. Therefore, it is of great importance to evaluate multi-component interactions together in the mix design process, to perform systematic compatibility analyses and to determine the appropriate component combinations accordingly. Although these studies provide significant findings, no common method has yet been proposed in the literature to holistically evaluate cement–SCM–SP compatibility, defining multi-component systems with a numerical index or a comprehensive metric. This makes

direct comparisons between different systems difficult and highlights the need for more comprehensive approaches to quantitatively measure compatibility.

Table 2.6 Overview of PC–SCM–SP compatibility studies

Study	Cement Type	SCM Type	SP Type	Test
Agarwal et al., 2000 [71]	OPC 33, 43, 53 grade, granulated blast furnace slag cement (PSC), Portland Pozzolana cement (PPC)	None (but PSC, PPC inherent)	PNS, Blended Polymer, PMS, LS	Setting time, Compressive strength, Differential thermal analysis
Erdogdu, 2000 [72]	Blended (KC 32.5), Pozzolanic (TC 32.5), Portland (PC 42.5)	None (but blended and pozzolanic inherent)	ASTM C494 Type F	Compressive strength
Hallal et al., 2010 [73]	CEM II 42.5	Limestone, Natural pozzolan	PNS, PMS	Fluidity (Marsh cone), Flow loss, SP saturation dosage
Burgos-Montes et al., 2012 [9]	CEM I 52.5 R	Limestone, Fly ash, Silica Fume	PNS, PMS, PCE, LS	Adsorption isotherm, Zeta potential, Rheology
Alonso et al., 2013 [74]	CEM I 42.5 R, CEM II/BL 32.5 N, CEM II/AV 42.5R, CEM III/B 32.5 R	Limestone, Fly Ash, Slag	Three PCEs with different carboxylic/ester groups ratios	Adsorption, Zeta Potential, Rheology, Conduction Calorimetry
Bahurudeen et al., 2014 [25]	OPC 53 grade	Sugarcane Bagasse Ash	PNS, PMS, PCE	Fluidity (Marsh cone, Mini-slump)
Zaribaf & Kurtis, 2018 [75]	ASTM C595 Type IL hydraulic cement	Metakaolin	PCE, LS, PNS, PMS	Workability, Isothermal calorimetry, Phase Evolution

				(TGA, XRD, Mini-slump)
Ting et al., 2019 [76]	OPC	Ultra fine slag	PCE	Setting time, Adsorption, Fluidity and fluidity loss, Rheology
Ibrahim & Meawad, 2022 [11]	CEM I 42.5 N	Waste glass powder	PNS, PCE	Setting time, Fluidity and slump retention, Adsorption, Zeta potential
Sposito et al., 2022 [12]	Portland Limestone Cement	Calcined clay (Kaolinite, Muscovite)	PCE	Rheology
Ding et al., 2023 [77]	OPC	Silica Fume	PCE	Fluidity, Saturation Point, Flexural and Compressive Strength
Chi et al., 2024 [78]	OPC	Muscovite (non-calcined)	PCE	Mini slump, Rheology, Adsorption
Xie et al., 2024 [79]	OPC	Coal Gangue Powder	PCE	Fluidity, Rheology, Compressive Strength

*PNS: poly-naphthalene sulfonate, PMS: poly-melamine sulfonate, PCE: polycarboxylate, LS: lignosulfonate

Agarwal et al. investigated the compatibility of different superplasticizers with various types of cement, focusing on their effects on setting time and compressive strength. The study revealed that ordinary Portland cement with a 33-grade exhibited significant retardation when used with naphthalene-based superplasticizers, whereas the

43-grade cement showed similar retardation with a blended polymer-based superplasticizer. In contrast, Portland slag cement and 53-grade ordinary Portland cement demonstrated compatibility with all tested superplasticizers. The hydration behavior of cement was analyzed using differential thermal analysis, confirming that certain superplasticizers delayed hydration, particularly in pozzolanic and lower-grade Portland cements. The study highlights the necessity of selecting an appropriate superplasticizer-cement combination to ensure optimal workability and strength development in concrete applications [80]. Focusing on its impact on compressive strength, Erdoğan examined how well ASTM C 494 Type F superplasticizer worked with various cement compositions. Three types of cement—blended cement, pozzolanic cement, and Portland cement—were investigated with different cement amounts and superplasticizer dosages. Though benefits beyond this dosage were restricted for blended cement, the data showed that a 3% superplasticizer produced the greatest strength increase. On the other hand, especially at early ages, pozzolanic and Portland cements showed a linear increase in strength associated with rising superplasticizer concentration. According to the study, cement type greatly affects the efficacy of superplasticizers; Portland cement shows the best compatibility with early strength development. The results highlight the need to maximize performance by optimizing superplasticizer dosage depending on the kind of cement [81]. Hallal et al. investigated the impact of limestone powder and natural pozzolan as partial substitutes for cement on the fluidity of blended cement paste, evaluating two superplasticizers with distinct chemical compositions. Melamine-based superplasticizers showed better compatibility in general, while polynaphthalene sulfonate-based superplasticizers showed superior fluidity and less fluidity loss with cement containing limestone dust. Mixtures containing natural pozzolan showed significant fluidity loss and required a higher dosage of superplasticizer. Addition of limestone dust to these mixtures increased fluidity due to dilution effect. As a result, it was emphasized that compatibility between cement and superplasticizer should be optimized for workability and rheological stability [73]. Burgos-Montes et al. investigated the compatibility of naphthalene-based, melamine-based, lignosulfonate-based and polycarboxylate-based superplasticizers with blended cements containing limestone, fly ash and silica fume by evaluating rheology, adsorption isotherms and zeta potentials. The adsorption and dispersion mechanisms of superplasticizers are significantly affected by the surface charge and specific surface area that change with the presence of SCMs. Different superplasticizers showed better compatibility results with

different SCMs. For example, fly ash showed more compatibility with melamine-based additives, while limestone showed more compatibility with polycarboxylate-based superplasticizers. Silica fume requires a higher dosage of superplasticizer to achieve sufficient fluidity due to its high surface area and negative zeta potential. Therefore, silica fume is more compatible with polycarboxylate-based superplasticizers that are effective at low dosages. This study emphasizes that superplasticizer selection should be made by taking into account the performance criteria (workability, water requirement, etc.) of cementitious systems according to the chemical and physical properties of the SCMs used [9]. Alonso et al. investigated the adsorption behavior, rheological properties, and hydration kinetics of polycarboxylate-based additives with Portland cement and three blended cements containing limestone, fly ash, and blast furnace slag. It was observed that polycarboxylate-based additives adsorbed on both cement particles and the surface of SCMs. Limestone showed the highest adsorption capacity, while cement containing slag showed the best plasticizer performance, although its adsorption decreased. However, hydration delay was observed more clearly in cement pastes containing blast furnace slag. Fly ash showed good fluidity performance despite its low adsorption capacity. This study emphasizes that the superplasticizer dosage should be selected and adjusted according to the cement content to ensure appropriate workability and compatibility in cementitious systems [74]. Bahurudeen et al. examined the interactions of two types of superplasticizers (polycarboxylate ether-based and naphthalene sulfonated formaldehyde-based) with sugarcane bagasse ash-based Portland pozzolana cement. of Sugarcane bagasse ash was used at three different substitution rates: 10%, 15%, and 20%. The results indicated that polycarboxylate ether-based superplasticizers exhibited superior compatibility with bagasse ash-blended cement compared to naphthalene-based superplasticizers. This was attributed to the enhanced dispersion and steric hindrance effects of polycarboxylate superplasticizers, which mitigated the adverse impact of the irregular silica particle structure in bagasse ash on fluidity loss. On the other hand, the higher dosage requirement of naphthalene-based superplasticizer is attributed to the increased adsorption and less electrostatic repulsion force on the cement surface [25]. Zaribaf and Kurtis studied the compatibility of four different superplasticizers (polycarboxylate ether (PCE), calcium lignosulfonate (LS), naphthalene formaldehyde condensate (PNS), and polymelamine sulfonate (PMS)) with Portland-limestone cements (PLC) containing metakaolin. Compatibility was evaluated based on workability, hydration properties, and phase evolution of the cementitious system. The experimental

methods used for compatibility evolution are mini-slump test, Thermogravimetric analysis (TGA), and X-ray diffraction (XRD). Although LS and PNS showed better compatibility at a high metakaolin substitution rate, PCE and PMS were found to have more positive effects due to loss of workability. Among the four superplasticizers, PCE is the most compatible additive due to its better dispersion effect and not disturbing the hydration. The appropriate superplasticizer type and dosage are very important for acceptable workability and hydration performance in blended cement systems [82].

Ting et al. investigated the effects of ultra-fine ground granulated blast-furnace slag (UFS) on cement pastes' initial setting time, fluidity, and rheological properties. UFS accelerated the setting by shortening the induction period, indicating that finer particles have a stronger accelerating effect. On the other hand, it negatively affected the fluidity, especially by increasing the UFS dosage and reducing the initial fluidity of the pastes. However, a synergistic effect was noted when using polycarboxylate superplasticizer, improving dispersion efficiency and fluidity retention. Rheological, UFS increased yield stress and plastic viscosity, but when used with polycarboxylate superplasticizer, this effect was eliminated by reducing shear stress and improving workability. Therefore, optimizing slag dosage and superplasticizer usage is critical to maintain fluidity and improve the performance of cementitious systems [76]. Ibrahim and Meawad studied the compatibility of waste glass powder with polynaphthalene sulfonate and polycarboxylate superplasticizers in ordinary Portland cement systems. The compatibility parameters were evaluated in terms of flowability, slump retention, adsorption behavior, and zeta potential in cement pastes containing 5%, 10%, and 15% waste glass powder. Polynaphthalene sulfonate showed better compatibility by increasing its dispersion and improving its flowability. On the other hand, polycarboxylate superplasticizers showed lower adsorption, leading to lower dispersion efficiency. Zeta potential analysis showed that polynaphthalene sulfonate improved electrostatic repulsion, stabilized the dispersion, while polycarboxylate primarily relied on steric hindrance. The findings indicate that the interaction between waste glass powder and superplasticizers is highly dependent on the type of mixture, and polynaphthalene sulfonate exhibited superior performance in maintaining workability and dispersion stability [11]. Ding et al. examined the effect of various sulfate types on the compatibility between polycarboxylate superplasticizers (PCE) and cement-based materials, particularly in the presence of silica fume. Five sulfates— Na_2SO_4 , K_2SO_4 , MgSO_4 , $\text{KAl}(\text{SO}_4)_2$, and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ —were assessed for

their influence on fluidity, mechanical properties, and salt precipitation. The study found that soluble sulfates (Na_2SO_4 and MgSO_4) exhibited the most detrimental effects on PCE dispersion, significantly reducing fluidity due to competitive adsorption between sulfate ions and PCE molecules on cement particles. In contrast, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ had minimal impact on fluidity, while K_2SO_4 and $\text{KAl}(\text{SO}_4)_2$ displayed moderate effects, primarily at higher dosages. Additionally, sulfate presence altered PCE saturation points, with soluble sulfates increasing adsorption demands. The study also highlighted that excessive sulfate concentrations led to salt precipitation of PCE, negatively affecting its dispersing efficiency. The findings underscore the need for careful sulfate control in cementitious systems to maintain workability, compatibility, and long-term stability when using PCE superplasticizers [77].

Achieving good compatibility between PC-SCMs-SPs can help to reduce PC content based on the results of the above-mentioned studies, therefore facilitating a change toward lower-carbon cement formulations without sacrificing workability, strength, or durability. A lower water-to-cement ratio results from improved dispersion efficiency and hydration control through the suitable superplasticizer dosage and selection, improving cementitious systems' entire performance. Studies have indicated that although their performance may be influenced by adsorption mechanisms, sulfate interactions, and hydration retardation, polycarboxylate-based superplasticizers typically give better dispersion and workability retention at lower dosages. On the other hand, since naphthalene- and melamine-based superplasticizers depend on electrostatic repulsion mechanisms, their dosages frequently call for higher values. Better compatibility also helps incorporate SCMs, lowering the dependency on high-clinker cement. Component compatibility is crucial since incompatibilities can cause problems such as too high slump loss, poor dispersion, delayed setting, or decreased strength, compromising concrete performance. Portland cement chemical and mineralogical composition, sulfate type and concentration, water/cement ratio, superplasticizer type, and dosage affect compatibility.

Ensuring stability, workability, and long-term performance of the system depends on understanding compatibility in cementitious systems. Affected by components like chemical composition, mineralogical properties, and hydration kinetics, the interactions among PCs, SCMs, and SPs are highly complex. Dealing with these interactions from one side and concentrating just on PC-SPs or PC-SCMs can result in an inadequate knowledge of the behavior of several components. For instance, changes in surface

chemistry, sulfate balance, and ion dissolution rates cause a superplasticizer that performs well in a Portland cement system to show lower efficiency or changed dispersion behavior when present with SCMs. Variations in C_3A concentration, sulfate availability, and alkali levels can similarly greatly influence the hydration process, therefore causing problems such as early stiffening, delayed setting, or instability in air entrainment. By changing pore structure, reaction kinetics, and long-term durability qualities, SCMs in the system further complicate these interactions. A holistic approach that considers the combined effects of all components allows for reductions in clinker content without compromising performance.

Despite the extensive literature on SCM-superplasticizer compatibility, there is a clear gap in comprehensive studies providing a holistic and systematic evaluation of these systems. Current approaches in literature typically evaluate compatibility based on isolated parameters such as flowability, setting time, hydration kinetics, compressive strength, rheology, or adsorption behavior. However, these discrete evaluations do not offer a unified framework that can systematically and flexibly compare different SCM-superplasticizer combinations.

The Multi-Criteria Compatibility Index (MCCI) proposed in this study addresses this gap by consolidating various performance criteria into a single, adjustable index. This approach allows researchers and practitioners to prioritize criteria based on application requirements and operational conditions, facilitating a holistic assessment of SCM-superplasticizer interactions. By providing a structured and comparative compatibility tool, the MCCI supports the development of more effective, low-carbon, and high-performance blended cement systems, and establishes a robust basis for future studies on SCM-admixture compatibility. Table 2.6 presents the current compatibility measures, their assessment methodologies, and inherent limitations, while illustrating how the MCCI framework effectively addresses these deficiencies. Although multiple measures are often utilized concurrently in literature, they are typically analyzed in isolation without a cohesive weighting system. The MCCI technique systematically integrates these diverse characteristics into a single index, enabling application-focused comparative assessments.

2.6 Machine Learning in Concrete and Cement Science

The transition from experience and intuition-based methods to data-driven techniques for advancing engineering systems is essential for accelerated innovation. In addition to minimizing expensive and time-intensive iterative testing, data science can address economic and sustainability limitations. Data-driven engineering can optimize circumstances to tackle issues in the field, such as the production of highly sustainable materials and enhancements in urban infrastructure. Machine learning (ML) is an umbrella term encompassing various effective algorithms used for data relationships, enabling the modeling and optimization of complicated systems [83].

Concrete is the most frequently produced human-made material on Earth and the second most commonly consumed commodity, following water. Concrete is a critical component of the construction industry because of its unique combination of durability, affordability, moldability, and strength, distinguishing it from other engineering materials such as steel, polymers, and wood. Concrete is the primary material used to construct various common infrastructure components, including buildings, roads, bridges, and structures. The world's annual consumption of concrete has exceeded 35 billion tons, twice the amount of all other construction materials combined. The scientific evolution of concrete research has unfolded across four fundamental paradigms, as demonstrated in Figure 2.4. The first paradigm, rooted in empirical methodologies, primarily relied on iterative experimental procedures to refine concrete mixture compositions. This approach involved systematic adjustments of constituent proportions, including cement, water, aggregates, and admixtures, until the desired performance criteria were met. However, large-scale optimization remained an inherent challenge due to its labor-intensive and time-consuming nature. The second paradigm, theoretical science, emerged in the 1980s, introducing microstructural modeling techniques that enhanced the fundamental understanding of cement hydration and its influence on material properties. By integrating principles from kinetics, thermodynamics, and mechanics-exemplified by frameworks such as CEMHYD3D and HYMOSTRUC-these, these models enabled the simulation of hydration reactions and the prediction of time-dependent behavioral characteristics of concrete. Despite these advancements, the reliance on empirical calibration and inherent limitations in generalizability across diverse material compositions constrained their broader applicability.

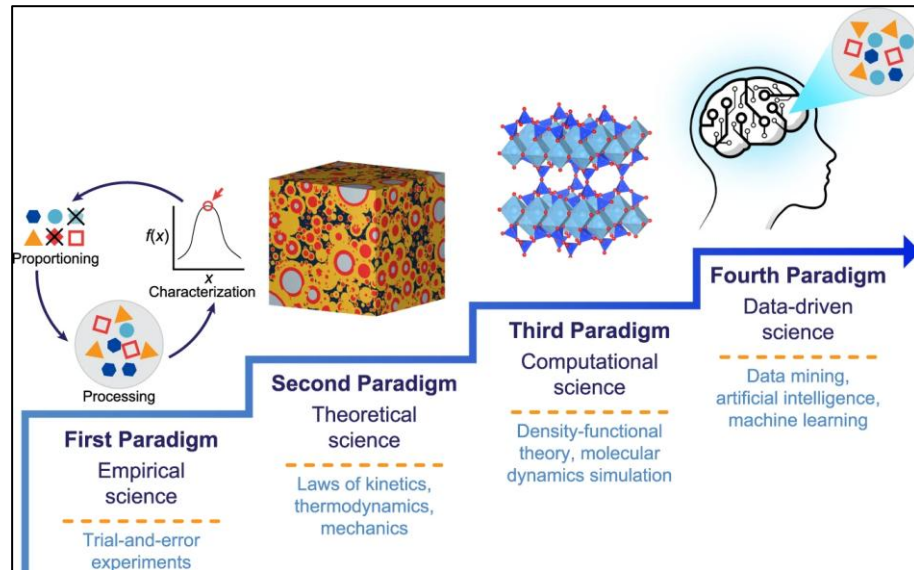


Figure 2.4 The evolution of concrete research from empirical to data-driven paradigms (Source: [26])

The third paradigm, computational science, gained momentum in the 2000s with the advent of high-performance computing. First-principles approaches, such as density functional theory (DFT) and molecular dynamics (MD) simulations, facilitated investigations at atomic and molecular scales, providing critical insights into the behavior of cementitious phases, particularly calcium silicate hydrate (C-S-H), the primary hydration product responsible for mechanical performance. Nevertheless, these computational techniques imposed significant demands on processing power and remained constrained by scalability and experimental validation challenges. The fourth and most contemporary paradigm, data-driven science, signifies a transformative shift by integrating artificial intelligence (AI) and machine learning (ML) methodologies. Despite ongoing developments in conceptual frameworks and methodological techniques in concrete science, the design of concrete with specific qualities continues to pose considerable difficulty due to the growing complexity of cementitious materials. ML has demonstrated its transformative capability in empirical research by independently tackling complex tasks. By leveraging extensive datasets derived from experimental and computational studies, ML models autonomously discern complex correlations between compositional variables and material properties, thereby mitigating the reliance on conventional iterative approaches. These data-centric strategies expedite the discovery of novel cementitious materials, enhance the predictive accuracy of process–structure–property interdependencies, and streamline concrete research and innovation. ML process

in concrete science typically includes six steps: problem definition, data collection, and data pre-processing to model development, model evaluation, and model deployment (given in Figure 2.5) [84].

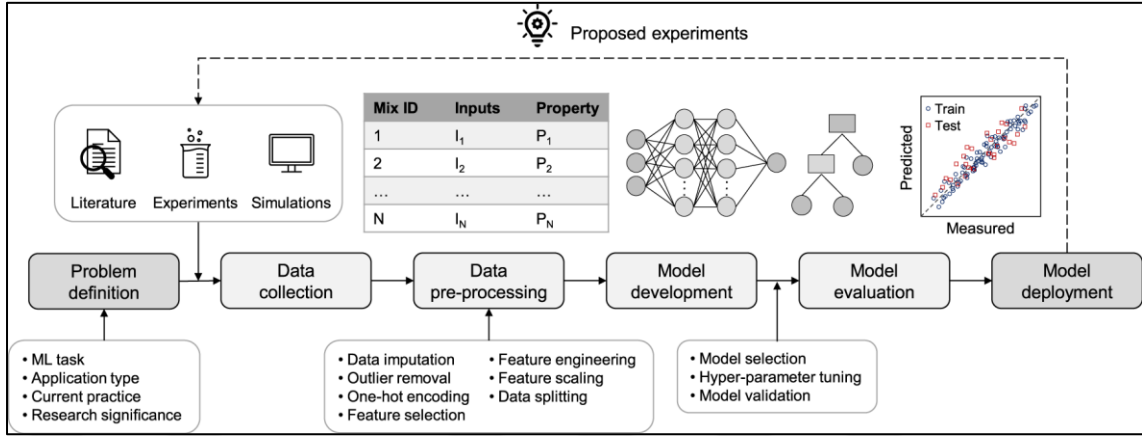


Figure 2.5 The typical process of machine learning in concrete science (Source: [26])

In recent decades, machine learning and artificial intelligence have been employed to predict material properties based on composition and synthesis parameters. "In the machine learning approach, models that optimize material properties are developed by inputting data into an algorithm. In numerous studies, machine learning has been utilized to predict the features of cementitious materials, representing an increasingly popular area of research [13]. According to published documents indexed in Scopus and containing the keywords "machine learning" and "cement" (searched within article title, abstract, and keywords), the number of studies has increased dramatically since 2014, as given in Figure 2.6. The following part provides a concise overview of key studies in literature, highlighting different models, input-output variables, and their applications.

Artificial neural networks (ANNs) were the foundation of the initial ML approaches in cement and concrete research. These algorithms are "black boxes" and employ statistical inference in a series of layers with weight-optimized nodes to establish links between material properties and composition. In 1998, Yeh utilized an artificial neural network (ANN) on a dataset comprising 1030 concrete samples from 17 sources. The features employed for predicting compressive strength included the compositional proportions of cement, supplementary cementitious materials (SCMs), aggregate, water, age, and admixture. The model demonstrated a coefficient of determination (R^2) exceeding 0.90 for both training and testing sets, surpassing the performance of traditional regression analysis [85]. Over the years, numerous machine learning algorithms were

applied to the dataset published by Yeh, evaluating their ability to predict compressive strength, resulting in the publication of several papers [86-88].

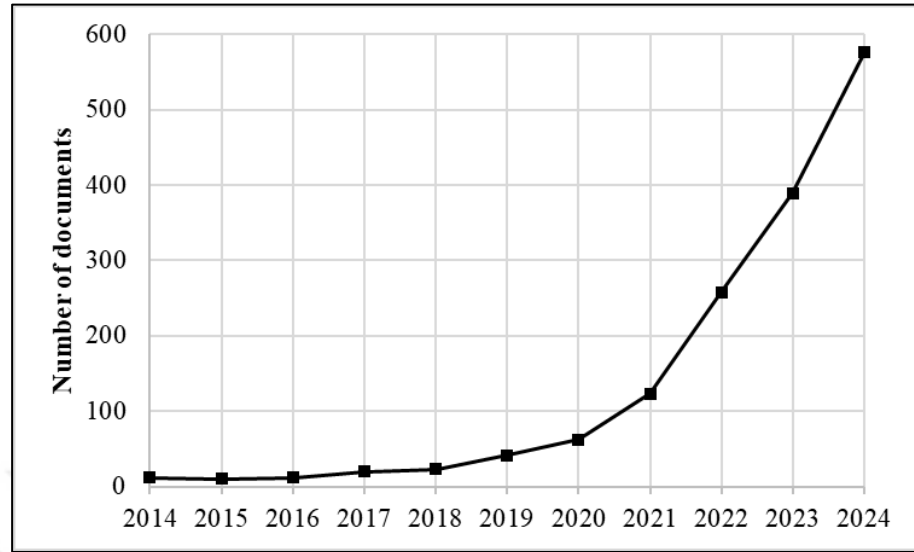


Figure 2.6 Number of documents published in Scopus between 2014-2024

Wang et al. (2012) developed a flexible neural tree (FNT) model to predict the early-age hydration kinetics of Portland cement, addressing the limitations of traditional analytical equations. The study utilized microcalorimetry experiments to collect data on heat release over time, forming a dataset of degree of hydration time series. The model was trained using Gene Expression Programming (GEP) and Particle Swarm Optimization (PSO), resulting in a high correlation between predicted and experimental hydration curves. Key influencing factors included cement chemical composition (CaO , SiO_2 , Al_2O_3 , Fe_2O_3 , SO_3), water-to-cement ratio (w/c), and reaction temperature. The results demonstrated that the FNT model effectively simulates hydration kinetics, providing a data-driven approach to understanding microstructure evolution in cementitious systems [89]. Lapeyre et al. (2021) developed a Random Forest (RF) machine learning model to predict the hydration kinetics of multicomponent cementitious systems using a dataset comprising 235 unique cementitious mixtures. The study utilized seven synthetic cements and three mineral additives (coarse limestone, fine limestone, and metakaolin) with varying physicochemical properties. Input variables included cement composition, additive type and content, and time, while the output parameters were cumulative heat release (J/g OPC) and heat flow rate (mW/g OPC) over a 24-hour period. The RF model demonstrated high predictive accuracy ($R^2 = 0.98$ for cumulative heat release, $R^2 = 0.91$ for heat flow rate), outperforming traditional reaction-kinetics

models. The model's ability to accurately predict hydration behavior and optimize mixture designs suggests that machine learning can be a powerful tool for accelerating the development of low-carbon cementitious materials [90]. Cook et al. (2021) demonstrated the effectiveness of machine learning (ML) in predicting the hydration kinetics of blended cement systems, addressing the limitations of traditional models. They trained a Random Forest (RF) model on 7800 records from 326 different cementitious systems. They tested it on 312 records from 26 different cementitious systems, utilizing inputs like cement type, additive content, specific surface area (SSA), and time. The model demonstrated exceptional accuracy in forecasting total heat release ($R^2 = 0.979$, RMSE = 14.398 J/g OPC) and heat flow rate ($R^2 = 0.932$, RMSE = 0.331 mW/g OPC) during a 24-hour period. Their findings indicate that machine learning can enhance mixture designs and forecast hydration behavior for novel formulations, hence promoting the creation of low- CO_2 cementitious materials via data-driven approaches [91]. Al-Hasani et al. (2023) developed a Gaussian Process Regression (GPR) model to predict the heat of hydration of cementitious systems, focusing on its application in mass concrete thermal modeling. The study utilized a dataset of 407 cementitious systems, incorporating 133 unique mix designs and variations at different temperatures. Input parameters included chemical composition (C_3S , C_3A , SO_3 , Na_2Oeq), Blaine fineness, water-to-solids ratio (w/s), curing temperature, and supplementary cementitious materials (SCMs) such as fly ash, blast furnace slag, and limestone. The GPR model achieved high accuracy ($R^2 = 0.972$, RMSE = 15.35 J/g) in predicting cumulative heat of hydration up to 72 hours, outperforming traditional kinetic models. Sensitivity analysis highlighted curing temperature, cement phase composition, and SCM content as key influencing factors. The model was further validated through mass concrete thermal simulations, confirming its reliability in predicting internal temperature development in large-scale concrete structures. These findings confirm the effectiveness of machine learning for optimizing thermal performance in concrete structures [92].

Canbek et al. (2022) explored the use of machine learning (ML) to predict the yield stress of limestone calcined clay cement (LC3) by establishing links between composition and hydration kinetics. The study analyzed 48 cement paste formulations, incorporating key parameters such as cement composition (PC:MK: LS ratio), water-to-solid ratio (w/s), limestone particle size, and gypsum content as input variables, with yield stress as the target output. Among the ML models tested, Support Vector Regression (SVR)

demonstrated the highest predictive accuracy ($R^2 = 0.967$, RMSE = 59.14 Pa). Feature selection analysis identified packing index (K), Al_2O_3/SO_3 ratio, total particle density (TPD), and MK/LS ratio as the most significant predictors of yield stress. A kernel smoothing method was also applied to hydration kinetics data, revealing a correlation between onset heat release and yield stress. These findings highlight the potential of ML-based approaches in optimizing LC3 mix designs, improving rheological properties, and facilitating the development of low-carbon cementitious materials [93]. Gao et al. (2024) developed a machine learning (ML)-based model to predict the rheological properties of 3D printable concrete (3DPC) using a dataset of 377 mix designs from 90 studies. The model utilized 19 input parameters, including binder types, water-to-binder ratio, sand-to-binder ratio, and admixtures, to predict static yield stress, dynamic yield stress, and plastic viscosity. An ensemble model (XGBoost + Neural Networks) achieved high accuracy ($R^2 = 0.917$ for static yield stress, 0.908 for dynamic yield stress, and 0.959 for plastic viscosity). SHAP analysis identified silica fume, viscosity modifying agent, and water content as key factors influencing rheology. The model successfully predicted unexplored mix designs, supporting data-driven optimization of 3DPC formulations [94].

Young et al. (2019) investigated machine learning (ML) models for predicting concrete compressive strength using a large dataset (>10000 observations) from industrial job-site mixtures. The study compared neural networks, random forests, gradient-boosted trees, and support vector machines (SVMs). The random forest performed best, achieving the lowest RMSE (4.4 MPa) and highest R^2 (0.60). The water-to-cement ratio, cement content, and admixtures are key influencing factors. The models successfully estimated 28-day compressive strength, enabling mixture optimization for cost and CO_2 reduction. This highlights ML's potential for enhancing concrete design efficiency and sustainability [95]. Salami et al. (2021) developed a machine learning approach for predicting the compressive strength of ternary-blend concrete, utilizing 1030 datasets compiled from 17 studies. The study compared the performance of the Least Square Support Vector Machine (LSSVM) optimized with Coupled Simulated Annealing (CSA) and Genetic Programming (GP). The LSSVM-CSA model achieved $R^2 = 0.954$ (train) and 0.923 (test), demonstrating its reliability in predicting compressive strength. Sensitivity analysis identified cement content, superplasticizer dosage, water-to-binder ratio, and curing age as the most influential factors. The findings highlight the potential of ML in enhancing mix design accuracy and reducing experimental workload in sustainable concrete

development [95]. El Khessaimi et al. (2023) applied ML to predict the compressive strength of limestone calcined clay cements (LC3) using a dataset of 323 mix designs (10692 data points). Fourteen input parameters were used, including cement composition, reactivity ratios, calcination, and hardening conditions, with compressive strength as the output. Among seven ML models tested, XGBoost showed the best accuracy ($R^2 = 0.99$ (train), 0.95 (test); RMSE = 11.4 MPa (test)). The alumina-to-silica ratio and hardening age were the most influential features. The model successfully predicted strength trends, supporting its use for LC3 optimization and low-CO₂ cement design [13]. Aslam and Shahab (2024) applied machine learning (ML) to predict the compressive strength of blended cement concrete using 1288 data points with 10 input variables (SCMs, water, aggregates, and superplasticizers). Among 11 ML models, XGBoost showed the highest accuracy ($R^2 = 0.90$, RMSE = 5.43 MPa). The water-to-binder ratio, fly ash, and cement content were the most influential features. The study confirms ML's potential for optimizing blended cement concrete mix design and reducing experimental workload in sustainable concrete research [96]. Babiker et al. (2024) utilized machine learning (ML) to predict and optimize the compressive strength of quaternary-blended cement concrete using a dataset of 810 mix designs. The study employed XGBoost (XGB), Random Forest (RF), and K-Nearest Neighbor (KNN) models, with XGB achieving the highest accuracy ($R^2 = 0.923$ for training and 0.997 for testing). The input parameters included cement, ground granulated blast furnace slag (GGBS), fly ash (FA), silica fume (SF), water, superplasticizers, fine aggregates, and coarse aggregates, alongside key mix design variables such as the water-to-binder ratio and curing age. Feature importance analysis indicated that curing age, water-to-binder ratio, and cement content were the most influential factors in predicting compressive strength. The study demonstrates the effectiveness of ML in optimizing mix proportions and enhancing the design of sustainable quaternary-blended cementitious materials [97].

Machine learning has emerged as a valuable tool in cement and concrete science, enabling the prediction and modeling of various material properties through diverse input parameters and extensive datasets. Machine learning methods have been extensively employed to assess critical properties such as hydration kinetics, rheology, and compressive strength, offering data-driven insights that advance material design and optimization. These models leverage experimental and computational databases to accurately represent intricate interactions among composition, processing conditions, and

performance, diminishing dependence on conventional trial-and-error methods. Additionally, ML is a practical approach for evaluating complex relationships within cementitious systems, facilitating more profound understanding and more efficient advancement.



Chapter 3

Experimental Methodology

3.1 Materials

The study used CEM I 42.5 R PC obtained from three different manufacturers. Furthermore, four types of SCMs were employed: natural pozzolan (NP), blast furnace slag (BFS), and two different calcined clays (CC). SCMs were supplied from different regions of Türkiye: NP from Kayseri/İncesu, BFS from Hatay/İskenderun; CC1 from Balıkesir/Düvertepe, and CC2 from Nigde/Hacıabdullah. NP was supplied in bulk form and afterward ground for two different durations, 60 and 120 minutes, using a ball mill. Since the BFS was already in a ground state, it was used in the experiments without additional processing. Both types of clay were finely ground in a laboratory ball mill for 45 minutes. After grinding, the clays were calcined at 700°C, maintained at this temperature for one hour, and then allowed to cool to room temperature inside the furnace. The chemical compositions of PCs and SCMs were determined by X-Ray Fluorescence (XRF) technique, and the results are presented in Table 1 and Table 2, respectively, along with their physical properties. The setting time and compressive strength tests were conducted in accordance with TS EN 196-3 and TS EN 196-1 standards, respectively. The results are consistent with the limits defined in TS EN 197-1 “Composition, specification and conformity criteria for common cements.”

Table 3.1. Chemical composition and physical properties of Portland cement

Chemical Composition (%)	PC1	PC2	PC3
SiO ₂	18.19	18.05	18.15
Al ₂ O ₃	5.16	5.00	4.50
Fe ₂ O ₃	3.07	3.01	3.27
CaO	64.48	63.55	62.61
SO ₃	2.69	2.40	3.14
MgO	2.14	1.70	3.06
Na ₂ O	0.32	0.72	0.40
K ₂ O	0.74	0.60	0.63
Loss on ignition	2.68	4.44	3.23
Physical Properties			
Specific gravity	3.14	3.13	3.15
Blaine fineness (cm ² /g)	3241	3660	3507
Initial setting time (min)	155	150	135
Final setting time (min)	205	220	190
Compressive strength of mortars			
2 days (MPa)	25.2	33.2	26.3
28days (MPa)	51.3	53.9	38.8

SCM particle size distribution was also determined by laser diffraction, shown in Table 3, with their particle diameter values where 10%, 50%, and 90% of the samples are smaller than those values (d_{10} , d_{50} , d_{90}). Also, X-Ray Diffraction (XRD) measurements were carried out with a diffractometer Bruker/Siemens XRD with a copper radiation $\text{Cu-K}\alpha = 1.54060 \text{ \AA}$. The data were collected between 5 and $65^\circ 2\theta$ angles. The step size was set to $0.02^\circ 2\theta$ per step. The software used to identify phases is Diffrac. Suite Eva. with PDF-2 database of International Centre for Diffraction Data (ICDD). XRD patterns and identified phases of the NP, BFS, CC1, and CC2 are indicated in Figure 3.1. As seen from the patterns (Figure 3.1 (a)), dolomite is the major crystalline phase in the natural pozzolan, and in BFS, the two main phases are calcite and mullite (Figure 3.1 (b)). Besides, the XRD pattern of CC1 (Figure 3.1 (c)) shows a mineralogical composition consisting of kaolinite and quartz as crystalline minerals, whereas CC2 contains kaolinite in addition to sanidine as well as an amorphous phase indicated by a raised background

of the pattern between 20° to 25° 2 θ angles (Figure 3.1 (d)). Similarly, natural pozzolan also contains an amorphous phase due to a background raising.

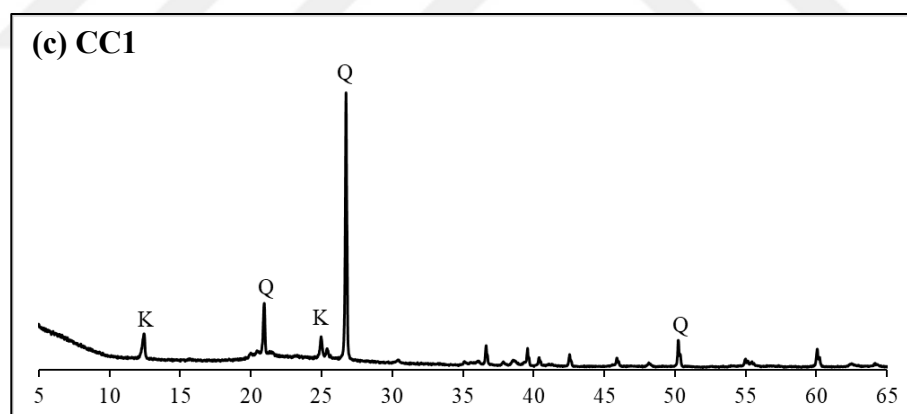
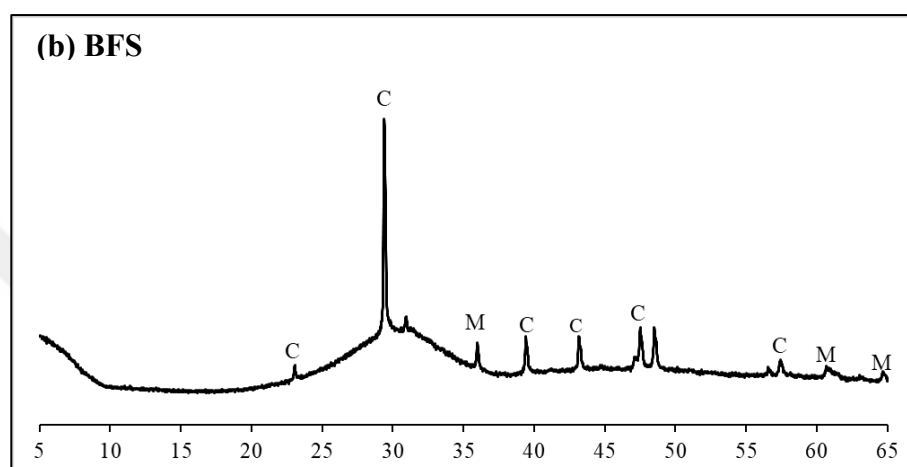
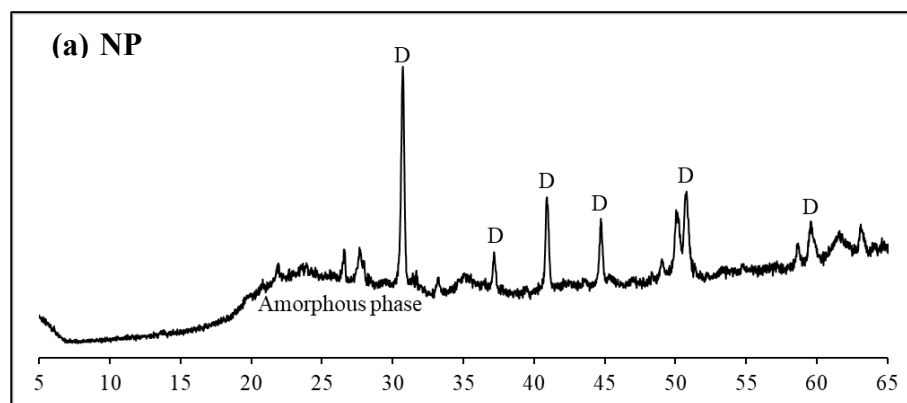
Table 3.2. Chemical composition and physical properties of SCMs

Chemical Composition (%)	NP		BFS	CC1	CC2
SiO ₂	71.21		36.80	58.94	62.47
Al ₂ O ₃	7.30		12.00	31.90	25.54
Fe ₂ O ₃	1.86		0.70	0.92	2.66
CaO	0.22		37.70	0.42	0.87
SO ₃	0.24		0.70	1.05	0.56
MgO	4.17		6.00	0.06	0.57
Na ₂ O	1.63		0.30	0.01	0.56
K ₂ O	1.45		0.70	0.21	1.35
TiO ₂	2.56		0.90	1.11	0.96
Mn ₃ O ₄	-		1.40	-	-
Loss on ignition	8.95		2.40	4.03	4.1
Physical Properties	60 min*	120 min*			
Water requirement (%)	108	113.0	-	107.0	113.0
Strength activity index, 7 day (%)	70.5	81.7	-	77.9	65.4
Strength activity index, 28 day (%)	85.0	93.7	-	102.1	84.3

*The values represent the grinding durations of the natural pozzolan in the ball mill.

Table 3.3. d₁₀, d₅₀, d₉₀ of SCMs

	d₁₀, μm	d₅₀, μm	d₉₀, μm
NP_60min	1.2	7.1	60.3
NP_120min	0.7	5.2	45.7
BFS	1.9	10.8	25.7
CC1	1.2	4	62
CC2	1.8	20	91



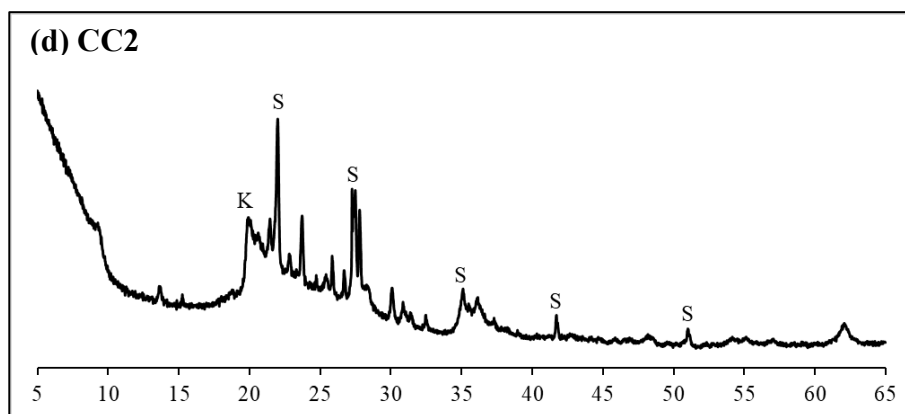
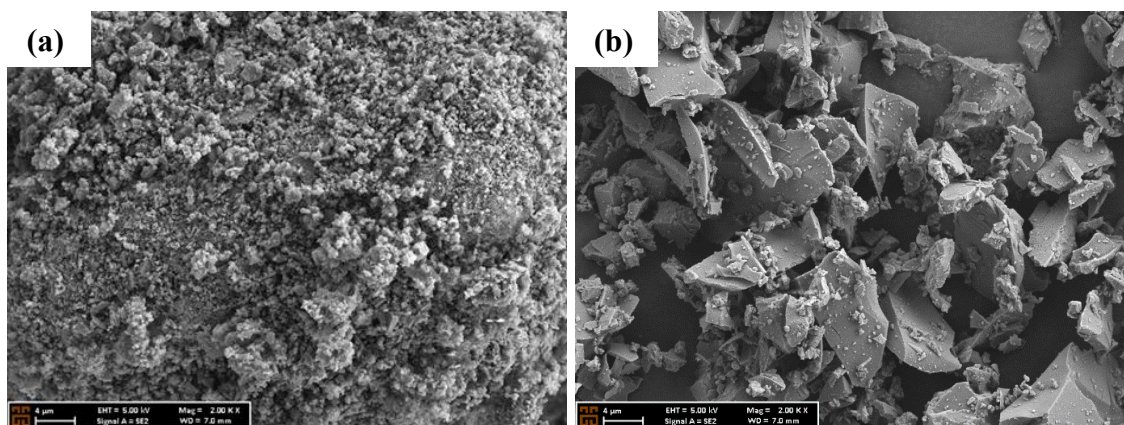


Figure 3.1 XRD patterns of (a) NP (D: Dolomite), (b) BFS (C: Calcite, M: Mullite), (c) CC1 (K: Kaolinite, Q: Quartz), and (d) CC2 (K: Kaolinite, S: Sanidine)

SCMs were analyzed using scanning electron microscopy (SEM) (ZEISS Gemini SEM 300) to examine their microstructure, with the micrographs presented in Figure 3.2. The samples were coated with 5 nm gold before analysis. Micrographs demonstrate that BFS consists of smooth, massive, and angular particles, while NP particles have textured surfaces (Figure 3.2 (a) and Figure 3.2 (b)). In Figure 3.2 (c) for CC1, a typical kaolinite structure with hexagonal plates is clearly observed. The SEM micrographs of CC2 revealed a distinct tubular structure attributable to the morphology of halloysite as a clay mineral.



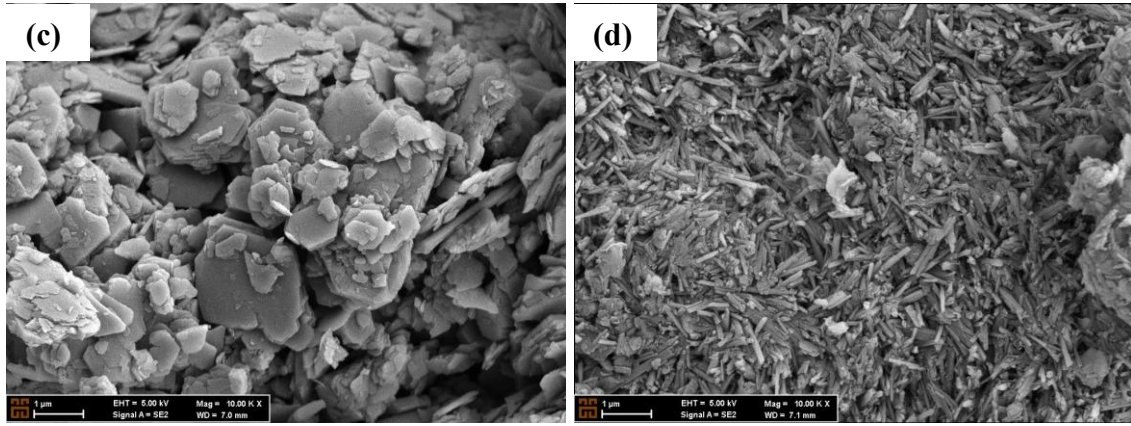


Figure 3.2 SEM micrographs of (a) NP, (b) BFS, (c) CC1 and (d) CC2

Three different commercially available superplasticizers were procured from BASF, Master Builders Solutions under the following trade names: poly-naphthalene sulfonate (PNS, EBA 1446), poly-melamine sulfonate (PMS, EBA 1710) and polycarboxylate (PCE, EBA 1447). Additionally, leonardite humic acid (LHA), which was developed in Abdullah Gül University laboratories as part of a completed TÜBİTAK 1001 project, was also included. SPs were applied in dry powder form and dissolved in pure water to eliminate the potential influence of additional chemical components in commercially available liquid SP formulations.

Leonardite to be used to produce humic acid-based superplasticizer was obtained from a commercially operated quarry in the Konya-Ilgın region (Figure 3.3 (a)). Homogenization studies were carried out before using the supplied raw material in the experiments. First of all, the powder sample was dried at 80 °C for 24 hours in order to remove the moisture content (Figure 3.3 (b)). Due to the negative effect of leonardite particle size on solubility in solution preparation, dried leonardite was ground in a ball mill for 30 minutes. The ground batches obtained were mixed in a large metal tray to ensure homogeneity. Then, the homogenized powder sample was kept in an airtight container for LHA production. The chemical composition of ground leonardite was determined by XRF analysis; the results are in Table 4. As seen in Table 4, some of the leonardite consists of organic content (45.69%), which is seen as the loss of ignition value in its chemical analysis. It was observed that the remaining inorganic impurities mainly consisted of SiO₂ and Al₂O₃. LHA was produced from ground leonardite using an alkali leaching method and a potassium hydroxide solution. The solution, which was stirred at 55 °C for 4 hours, was then centrifuged at 2000 rpm for 25 minutes, and the remaining solution was used as LHA (Figure 3.3 (c) and Figure 3.3 (d)).



Figure 3.3 (a) Leonardite raw material, (b) Ground leonardite, (c) LHA production process, (d) Final product LHA

Table 3.4. Chemical composition of leonardite

Chemical Composition	Leonardite
SiO ₂	30.75
Al ₂ O ₃	15.41
Fe ₂ O ₃	2.42
CaO	1.11
SO ₃	2.61
MgO	0.42
Na ₂ O	0.38
K ₂ O	-
Loss on ignition	45.69

3.2 Mix Design

In order to evaluate the compatibility parameters holistically and create a comprehensive dataset, different Portland cements, SCM type, SCM substitution rate, SCM fineness, water/binder (w/b) ratio, SP type, SP dosage, test time were systematically changed as shown in Table 3.3. Since the experiments conducted in the thesis study have different requirements, the water/binder ratio was selected and used according to the experiments. The mixing variables for cement pastes used in all experiments are presented in detail in Table 3.3.

So as to clearly understand the effects of the superplasticizers used and to evaluate them more accurately, the superplasticizer dosages were determined by adopting the equivalent dosage system. Thus, it was aimed to determine the effects of the additive, which is effective at lower dosages compared to other superplasticizers such as PCE, more correctly. The equivalent dosages determined by the mini-slump test will be given in the results section.

As a result, the total number of experiments conducted on cement paste mixtures prepared with the variables given separately for all experiments in Table 3.3. Total number of paste mixtures tested for isothermal calorimetry, thermal analysis, and compressive strength was 310, 217 and 144, respectively. Since the samples were tested on two different days for thermal analysis and four different days for compressive strength, the total number of samples were 434 and 576 for thermal analysis and compressive strength, respectively. .

Table 3.5. Mixing variables of cement pastes according to experiments

	PC type	SCM type	SCMs substitution rate (%)	SCM fineness	w/b ratio	SP type	SP dosage	Test time
Isothermal calorimetry	PC1, PC2, PC3	NP, BFS, CC1, CC2	NP: 20%, 30%, 40% BFS: 20%, 40%, 55% CC1: 20%, 30%, 40% CC2: 20%, 30%	NP: 60 min, 120 min BFS: unground CC1: 45 min CC2: 45 min	0.35, 0.40, 0.45, 0.50, 0.55	PNS, PMS, PCE, LHA	Equivalent dosages determined by mini-slump test	72 hours
Thermal Analysis	PC1, PC2	NP, BFS, CC1, CC2	NP: 20%, 30%, 40% BFS: 20%, 40%, 55% CC1: 20%, 30%, CC2: 20%, 30%	NP: 60 min, 120 min BFS: unground CC1: 45 min CC2: 45 min	0.40, 0.45, 0.50, 0.55			3, 28 days
Compressive strength	PC1, PC2	NP, BFS, CC1	NP: 20%, 30%, BFS: 20%, 40%, 55% CC1: 20%, 30%,	NP: 60 min, 120 min BFS: unground CC1: 45 min	0.40, 0.45, 0.50			2, 7, 28, 90 days

3.3 Test Methods

3.3.1 Mini-Slump Test

The mini-slump test determined the equivalent superplasticizer dosages required for blended cement pastes with three different water/binder ratios (0.35, 0.45, 0.50, and 0.55). The mini-slump test setup used in this study is a downscaled Abrams cone geometry, shown in Figure 3.4. (a), as suggested in previous studies in literature, 19 mm upper diameter, 38 mm lower diameter, and 57 mm height [98, 99]. Blended cement pastes were prepared by pre-mixing the dry powders (PC and SCM), which were performed prior to mixing with the water and superplasticizers. For each mini-slump test, 100 g of dry powder was combined with the specified amount of deionized water and superplasticizer. Since the sample amount was small, the mixtures were mixed with a hand mixer for 2 minutes. The homogeneously mixed paste was immediately used for mini-slump testing. To minimize inertial effects, freshly prepared paste was immediately put into the cone, and the cone was lifted as slowly as possible. Then, the spread diameter was determined by averaging two perpendicular measurements taken using a digital caliper (Figure 3.4 (b)).

PCE based superplasticizers have high water reduction capability at lower dosages compared to PNS, PMS and LHA. When PCE-based superplasticizers and other superplasticizers are used in equal dosages, it is not possible to make meaningful comparisons for all experiments. The mini slump test was used to determine the superplasticizer dosages to be used in the study based on the equivalent plasticizing capability. First, the mini-slump values of cement pastes prepared at three different water/PC ratios given in Table 3.6 were determined. Then, at the same water/binder ratios, the required superplasticizer dosages were determined to bring the blended cement pastes (e.g. 20% SCM+80%PC; 40%SCM+60% PC; 55%SCM+45%PC) to the mini-slump values (range of ± 0.5 cm) given in Table 3.6.

Table 3.6. Mini slump test results for three different Portland cements at different water/PC ratios

Mini slump, cm			
water/PC	PC1	PC2	PC3
0.40	6.0	7.0	6.5
0.45	7.6	8.3	8.0
0.50	10.5	11.0	10.6
0.55	12.5	13.2	12.8

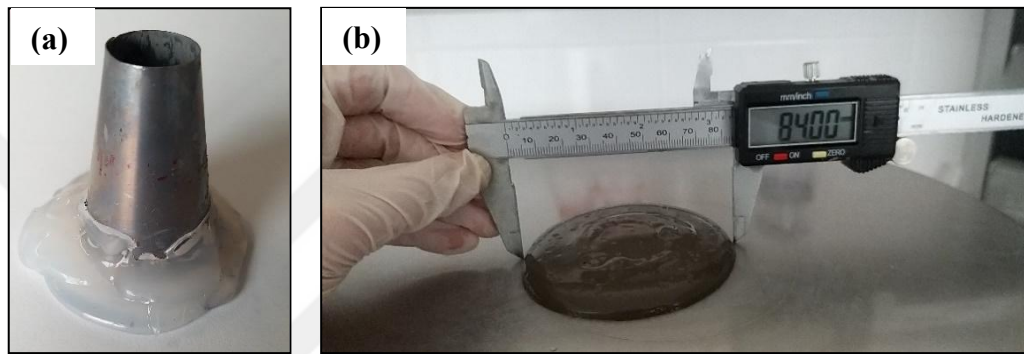


Figure 3.4 (a) Mini-slump cone, (b) Measurement of mini-slump diameter

3.3.2 Isothermal Calorimetry

Isothermal calorimetry was performed on cement pastes using a TAM Air Microcalorimeter device, TA Instruments (Figure 3.5 (a)), at 25 °C for 72 hours to observe hydration kinetics. Cement pastes were prepared by manually mixing with deionized water. Four different water/binder ratios (0.35, 0.45, 0.50, and 0.55) were used when preparing all cement pastes. Prepared samples are quickly placed in plastic ampoules of the isothermal calorimeter, as shown in Figure 3.5 (b). The rate of hydration (thermal power) was recorded in mW/g PC for 72 hours. The cumulative heat of the reaction of the pastes was obtained through integration as area-time data under thermal power.

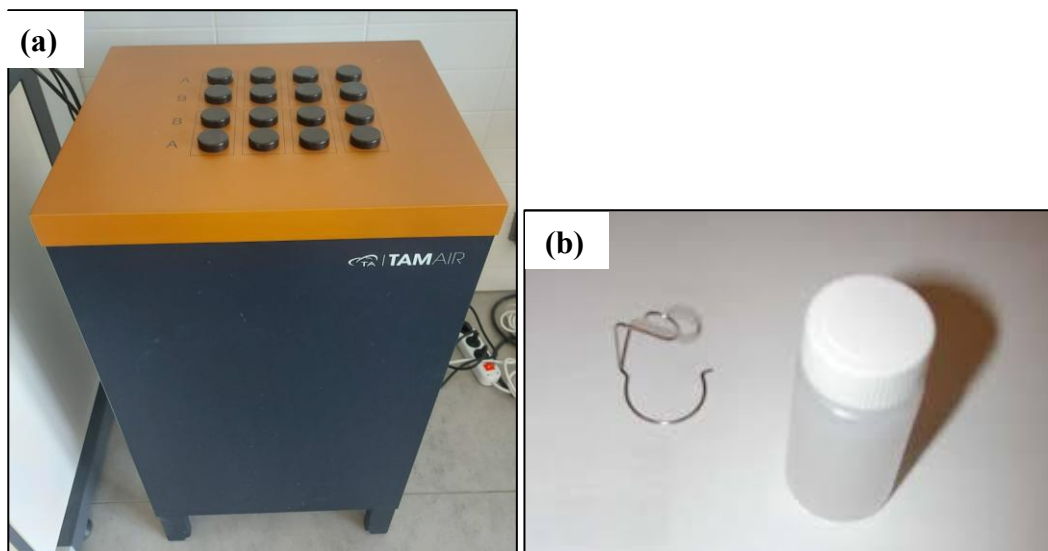


Figure 3.5 (a) TAM Air Isothermal Calorimeter device, (b) Plastic ampoule used in isothermal calorimeter

3.3.3 Thermal Analysis

Thermal analysis (TGA) of cement pastes prepared with three different water/binder ratio-0.45, 0.50, 0.55- for 3 and 28 days of age was performed. The cement pastes were prepared using the same procedure for the isothermal calorimetry samples. The cement pastes to be prepared for the analysis to be carried out on the hardened cement pastes were placed in plastic syringes to be stored without moisture loss and air contact until the test days. The syringes were stored in the climatic chamber at room temperature until the day of testing. The hardened cement pastes were taken from plastic syringes at specified ages, and the samples were analyzed in the DTG-60H Shimadzu thermal analysis device, as shown in Figure 3.6, over a temperature range from room temperature to 1000 °C with a temperature rise rate of 15 °C/min, under a nitrogen purge gas flow rate of 100 mL/min.

The hydration kinetics and pozzolanic reactivity in cement pastes were evaluated by measuring the free Ca(OH)_2 (CH) contents at various ages. Thermogravimetric analysis (TGA) measures the weight changes in cement paste due to increasing temperature. The amount of weight loss that results from the decomposition of Ca(OH)_2 and the evaporation of water in its structure between 400-600 °C can be used to determine the amount of Ca(OH)_2 in a hardened cement paste. The calculation of CH involves attributing mass loss in this region to the release of bound water, which is subsequently converted to CH content using a stoichiometric factor of 4.11 (calculated as: CH molar

mass/ H_2O molar mass: $74\text{g. mol}^{-1} / 18\text{g. mol}^{-1} = 4.11$). Nonetheless, due to the fact that the decomposition of C-S-H gel initiates at reduced temperatures and partially overlaps with the beginning of CH decomposition, the baseline slope obtained from the beginning of C-S-H decomposition is employed to calculate the mass loss. Thus, only the mass loss associated with CH decomposition is considered in the calculation. Finally, the CH content is expressed as a percentage relative to the mass of the paste ignited at $1000\text{ }^\circ\text{C}$, at which time all volatile compounds in the hardened cement paste are completely decomposed.

In this study, while calculating the CH content determined by the TGA method, the approach of normalizing the measured CH amount according to the PC amount in the mixture was applied. For example, if there is 80% PC content in the mixture, the measured CH content was normalized by dividing it by 0.8. The reason for applying this method is that the binder content in the mixture changes due to the replacement of cement by SCMs used in different ratios in the mixtures and therefore the measured CH amount varies depending on the PC ratio in the binder. Thanks to the normalization process, it becomes possible to compare CH consumption between mixtures with different replacement levels and the measured CH values are placed on a standard reference based on PC. Thus, a correct and fair comparison is made in evaluating the CH content, pozzolanic reactivity and hydration performance. Additionally, relative CH contents were calculated based on the normalized CH values, and these relative values were used as outputs in the regression analyses performed within the scope of this study. This approach was adopted to clearly reflect the pozzolanic reactivity and CH consumption performance of SCMs in different mixtures independent of the absolute CH amounts, ensuring that the predictive models developed in this study would be based on a consistent and comparable output parameter.

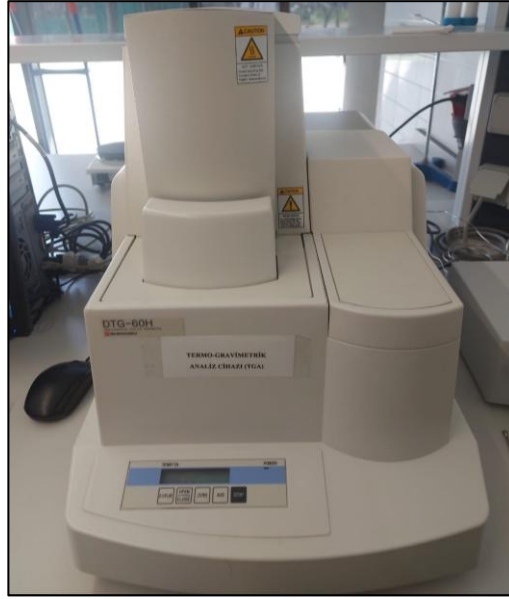


Figure 3.6 DTG-60H model thermogravimetric analysis (TGA) device

3.3.4 Compressive Strength

Cement pastes prepared for compressive strength were prepared by taking ASTM C305 as a reference. The aim of the standardized procedure throughout the thesis study was to ensure the homogeneity of the cement pastes and to increase experimental reproducibility. Hobart laboratory mixer was used for this entire mixing procedure. The mixing procedure is outlined step by step below.

- Firstly, dry materials PC and SCM were homogenized in one container. Water and superplasticizers were mixed in a separate container.
- The water-SP mixture was added to the mixing container, and then the dry mixture was added. It was waited for 30 s for the cement to absorb the water.
- The mixer was first operated at low speed - 140 ± 5 rpm - and mixing was carried out for 30 seconds.
- The mixer was stopped for 30 seconds, and the cement paste adhering to the container walls was homogenized by manual mixing.
- Finally, the mixer was operated at high speed (285 ± 10 rpm) and mixed for 60 seconds.

The prepared mixture was gradually filled into disposable plastic Ø34x60 mm cylinder containers so that no air was entrapped within the paste. Disposable and smaller sample containers were preferred primarily because of the high number of specimens to be prepared. Additionally, larger molds would have increased the material requirement

and posed challenges in obtaining certain SCMs. The compressive strength of pastes was tested at 2, 7, 28, and 90 days. Two cylindrical samples were prepared for each testing age, and the compressive strength average of these two samples was calculated. The hardened cement pastes removed from the cylindrical mold on the test day are shown in Figure 3.7.



Figure 3.7 Cylindrical compressive strength test samples

Compressive strength tests were performed on hardened cement paste samples. The load was applied to the mold-contact surfaces without using any bedding material. Each sample was centered under the loading head and was free to tilt for uniform contact. In order to ensure equal and balanced load distribution, tests were carried out with the smooth surfaces of the samples facing upwards. A constant loading rate of approximately 900 N/s was applied until failure.

Chapter 4

Computational Methodology

4.1 Overview of the Computational Approach

The use of admixtures (SCMs and/or superplasticizers) in cementitious systems challenges the prediction of the increasingly complex performance characteristics of blended cement. Therefore, more advanced computational techniques are required to develop prediction equations. Machine learning, as a new and emerging tool, will be used for regression analysis to determine the interrelationships between the characteristic parameters that govern the compatibility of the components with the help of MATLAB software (version R2022a). Regression models will describe the relationship between a response (output) variable and one or more predictor (input) variables.

The complexity of cause-and-effect relationships due to the high number of parameters and interactions makes it very advantageous to use machine learning tools as an innovative approach to this complexity. It is thought that this will facilitate a better understanding of the compatibility parameters, which are the focus of the thesis, and the design of component types and compositions of low-carbon, high-performance blended cement. In this study, experimental outcomes derived from isothermal calorimetry, thermal analysis, and compressive strength measurements were evaluated using machine learning techniques. The adopted methodology allowed for the systematic investigation of various parameters affecting hydration kinetics, pozzolanic activity, and mechanical performance. As a result, a comprehensive evaluation metric—defined as the Multi-Criteria Compatibility Index (MCCI)—was developed as a key component of this thesis, designed to combine several performance criteria into a unified compatibility assessment framework.

4.2. Dataset Collection

The datasets used in the study were created based on the results obtained from isothermal calorimetry, thermal analysis, and compressive strength experiments. These experimental data reflect different performance parameters such as hydration kinetics, pozzolanic activity, and mechanical strength of cement-based systems. The variety of the dataset was achieved by considering different types of cement, SCMs, and SPs, as well as variable material properties and mixing ratios. This comprehensive data structure allows machine learning models to learn multidimensional relationships accurately.

As presented in Section 3.2, where the variables are presented in detail, the dataset consists of outputs obtained from a total of three different experimental methods, namely isothermal calorimetry (310 samples), thermal analysis (217 samples), and compressive strength (144 samples). The regression analysis establishes the underlying input-output relationships from the training dataset. Input and output variables were determined for each experimental data set, and these determined variables are presented below.

During the isothermal calorimetry results analysis, 7 inputs, and 4 different outputs were evaluated. The input variables are: OPC content (%mass); SP type; SP content (%); SCM d_{50} (μm); water/binder ratio; SCM $\text{SiO}_2+\text{Al}_2\text{O}_3$ content (%) and SCM CaO (%) content. The outputs are onset time (min), onset heat (mW/g cement), induction period (min), and total heat at 72 h (J/g cement). TGA results analysis, a total of 7 inputs and 2 different outputs were evaluated. The input variables are: OPC content (%mass); SP type; SP content (%); SCM d_{50} (μm); water/binder ratio; SCM $\text{SiO}_2+\text{Al}_2\text{O}_3$ content (%) and SCM CaO (%) content. The outputs are relative CH content normalized as PC amount at 3-day (%) and 28-day (%). Finally, compressive strength results analysis, a total of 6 inputs and 4 different outputs were evaluated. The input variables are OPC content (%mass), SP type, SP content (%), SCM d_{10} (μm), water/binder ratio, and SCM $\text{SiO}_2+\text{Al}_2\text{O}_3$ content (%). The outputs are compressive strength at 2, 7, 28, and 90 days (MPa).

The minimum, maximum, and mean values shown in Tables 4.1 and Table 4.2 demonstrate the complexity underlying predicting the behavior of cementitious systems. For example, while the OPC content in isothermal calorimetry varies between 40–100%, it is in the range of 45–100% in compressive strength tests, indicating that both control

samples containing only PC and blended cement mixtures were examined. The SCM particle sizes (d_{50} and d_{10}) exhibit a limited range (4–20 μm and 0.7–1.9 μm), whereas chemical parameters like $\text{SiO}_2 + \text{Al}_2\text{O}_3$ and CaO demonstrate a wide distribution, illustrating the variety of SCM types with distinct chemical characteristics used. Although the SP content averages only ~0.5–0.6%, compared to its maximum values, the additives can substantially influence both the fresh and hardened properties. The compositional differences and variations in water/binder ratios and superplasticizer dosages create a multidimensional parameter space that complicates prediction models.

When Tables 4.1 and Table 4.2 are examined, it is shown that there is wide variability in both chemical and physical inputs in each of the isothermal calorimetry, thermal analysis, and compressive strength datasets. The OPC, SP, and SCM contents and water/binder ratios show different ranges in each dataset, especially since the variety in the chemical composition of SCMs complicates the modeling process. In the output variables, the wide ranges between the minimum and maximum values in hydration kinetics, CH content, and compressive strength indicate that the system response has a multivariate and non-linear structure. In addition, the fact that the mean values are generally not close to the maximum values indicates that the data are mostly clustered in lower ranges and that the extreme values represent only a limited part. This situation presents a critical requirement for the models to capture general trends and learn rare extreme cases and low-density patterns correctly. Therefore, the selection and implementation of machine learning methods should be carefully designed and implemented to handle the heterogeneity and complexity of the data set effectively. Also, the detailed statistical summaries of the variables used in the modeling process are provided in the Appendix. These tables report the minimum, maximum, and mean values of the input variables for the full dataset presented in this section, as well as for the training (80%) and test (20%) splits. Presenting these descriptive statistics separately allows the distributional characteristics of each partition to be examined. In addition, the Appendix includes a corresponding table for the output variables, enabling a direct comparison across all subsets. Overall, the summary statistics indicate that the training and test sets exhibit highly similar numerical ranges and central tendencies, confirming that the data split preserves the underlying distribution of both the input and output variables.

Each experimental dataset was evaluated independently within its context, and the appropriate input-output parameters were determined. This approach was preferred because different experimental techniques reflect different physical and chemical processes. For example, the fineness parameter was represented by the SCM d_{50} value in the context of isothermal calorimetry and TGA because it is known to affect reactivity and early-age hydration behavior in these analyses directly. In contrast, the SCM d_{10} value was used in compressive strength because the effect of finer particles on strength development is more pronounced. In this context, each experimental dataset was adjusted according to its specific objectives and prepared according to the machine learning models.

Table 4.1 Minimum, maximum, and mean values of input variables for the full datasets

Dataset	Input Variable	Min	Max	Mean
Isothermal Calorimetry	OPC (%)	40	100	68.6
	SP (%)	0.03	2.0	0.6
	SCM d_{50} (μm)	4.0	20.0	8.1
	Water/binder ratio	0.35	0.55	0.50
	SCM $\text{SiO}_2 + \text{Al}_2\text{O}_3$ (%)	49.5	91.76	75.1
	SCM CaO (%)	0.2	37.7	10.2
Thermal Analysis (TGA)	OPC (%)	45	80	70.5
	SP (%)	0.03	1.7	0.6
	SCM d_{50} (μm)	4.0	20.0	9.2
	Water/binder ratio	0.40	0.55	0.50
	SCM $\text{SiO}_2 + \text{Al}_2\text{O}_3$ (%)	48.8	90.8	73.9
	SCM CaO content (%)	0.2	37.7	10.4
Compressive Strength	OPC (%)	45	100	73.0
	SP (%)	0	1.54	0.50
	SCM d_{10} (μm)	0.7	1.9	1.4
	Water/binder ratio	0.4	0.5	0.5
	SCM $\text{SiO}_2 + \text{Al}_2\text{O}_3$ (%)	48.8	90.8	70.2

Table 4.2 Minimum, maximum, and mean values of output variables for the full dataset

Dataset	Output Variable	Min	Max	Mean
Isothermal Calorimetry	Onset time (min)	60	1542	169.3
	Onset heat (mW/g cement)	0.25	2.30	0.90
	Induction period (min)	40.0	1100.0	175.5
	Total heat at 72 h (J/g cement)	112.0	451.0	346.7
Thermal Analysis (TGA)	Relative CH content at 3 days (%)	27.5	114.5	81.7
	Relative CH content at 28 days (%)	0	88.0	53.6
Compressive Strength	@ 2 days (MPa)	4.2	28.0	13.7
	@ 7 days (MPa)	9.3	42.6	22.7
	@ 28 days (MPa)	15.9	52.7	31.1
	@ 90 days (MPa)	17.1	54.3	34.3

4.3. Data Splitting and Preprocessing

Experimental datasets were randomly split into training and testing subsets using MATLAB software to evaluate model performance and generalizability. The split ratio was 20% test - 80% training. A 30/70 test/train split was also tested during preliminary studies and showed poorer prediction performance. Therefore, a 20/80 test/train split was applied for all datasets to provide more stable and generalizable results. Since the total number of experiments was different from each other, splitting operations were performed entirely separately for each experiment. In addition, in order to ensure the consistency of the results to be evaluated for each experiment, the selected test/training splits were kept constant. For example, in isothermal calorimetry data, all outputs of "onset time," "onset heat," "induction period," and "total heat at 72 hours" were evaluated using the same training and testing split.

Since the datasets consist entirely of experimental data, no data deletion, modification, or artificial correction was applied. Outlier analysis, which is usually applied when creating datasets, is the process of determining data points that statistically significantly deviate from the values in the dataset. However, outlier analysis was not

deemed necessary in this study, and it is assumed that all values obtained are a natural result of experimental variation and do not contain any systematic error. Consequently, no correction, deletion, or exclusion process was applied to the data sets; all data were used in their original form.

Since the dimensions of the input features are different, normalization is typically applied to ensure that no single variable dominates the learning process due to its magnitude. In preliminary analyses, the Min-Max scaling normalization method, which is a widely used method for normalizing data, was used. Each feature undergoes a transformation where the minimum value is converted to 0, the maximum value is converted to 1, and all other values are converted to decimals ranging from 0 to 1 [100]. However, after the normalization was applied, a decrease in the prediction performance of the models was observed. This decrease in performance is thought to be because the original data had values very close to each other, and the model's ability to distinguish significant but small differences decreased due to the narrowing of the data distribution after normalization. Therefore, throughout the study, all data was used without any normalization. Besides, to ensure the proper functioning of the machine learning model, one-hot encoding was implemented to convert the categorical data of the "superplasticizer type" into a numerical form.

4.3.1. Correlation Matrix

The relationship between N variables is described using correlation matrices. It is a square symmetric $N \times N$ matrix with the (ij) components equal to the coefficient of correlation R_{ij} between the (i) th and (j) th variables. Diagonal elements (correlations between variables) are always equal to one. The correlation matrix is a matrix that is constructed by aggregating the coefficient of correlation between pairs of characteristics in a dataset. There are numerous methods available for determining correlation coefficients. Pearson, the most frequently employed statistical measure, is the correlation coefficient. Nevertheless, it is important to acknowledge that it just evaluates linear relationships between two parameters. Example: A negative linear relationship is denoted by -1 between any two variables, whereas 0 indicates no relationship between the identified variables. However, a value of $+1$ indicates a positive correlation between the two variables [101].

Before developing the machine learning models, correlation matrices were used to analyze the relationships between the input variables in the dataset. This analysis was performed to identify variable pairs that showed particularly high linear relationships and to prevent possible multicollinearity problems. Pearson correlation coefficients were calculated for each experimental dataset (isothermal calorimetry, thermal analysis, and compressive strength) to evaluate the linear relationships among all input variables. Correlation matrices provide information about the relationships between variables and are also an effective tool for feature selection. In particular, after determining the variable pairs with a correlation coefficient of $|r| > 0.70$, only one of these variables was kept, and the others were removed from the inputs in order to prevent information duplication in the model. In this way, the inputs in the model were independent of each other, and the risk of overfitting was prevented.

4.4. Regression Model Development

Machine learning-based regression analyses enable mathematical description and prediction of complex relationships between many inputs and outputs. In this context, various regression modeling approaches were tested, and their performances were compared for all experimental datasets (isothermal calorimetry, thermal analyses, and compressive strength) used in the study. The regression learner toolbox of MATLAB software is one of the most frequently used techniques for regression. MATLAB (version R2022a) software was used in the regression analysis of this study. MATLAB's Regression Learner app is accessible from the APPS ribbon and is used to train regression models to predict data. It can also be directly called from the command Regression Learner. Using this application, data can be examined, models can be trained, and results can be evaluated. This application also has the option to "perform automatic training" to search for the best regression model, including linear regression models, regression trees, Gaussian process regression models, support vector machines (SVM), regression tree ensembles, and neural networks. Throughout the study, 29 regression models were tested with the models of six different regression classes (linear regression models, regression trees, Gaussian process regression models, support vector machines, ensembles of regression trees, and neural networks) in the MATLAB software. The regression classes available in MATLAB software and the models of these classes are shown in Figure 4.1.

The two model classes that generally provided the highest prediction accuracy were identified by evaluating each regression model class. The results were presented in detail after selecting one model with the greatest performance from each of these two classes. The main reason for presenting the results of only the most successful models instead of reporting all models separately was to increase the study's focus and allow the reader to compare the general trends of different model types more clearly. It was also anticipated that a detailed analysis of the poorly performing models would unnecessarily expand the scope of the study and cause ambiguity in the results section.

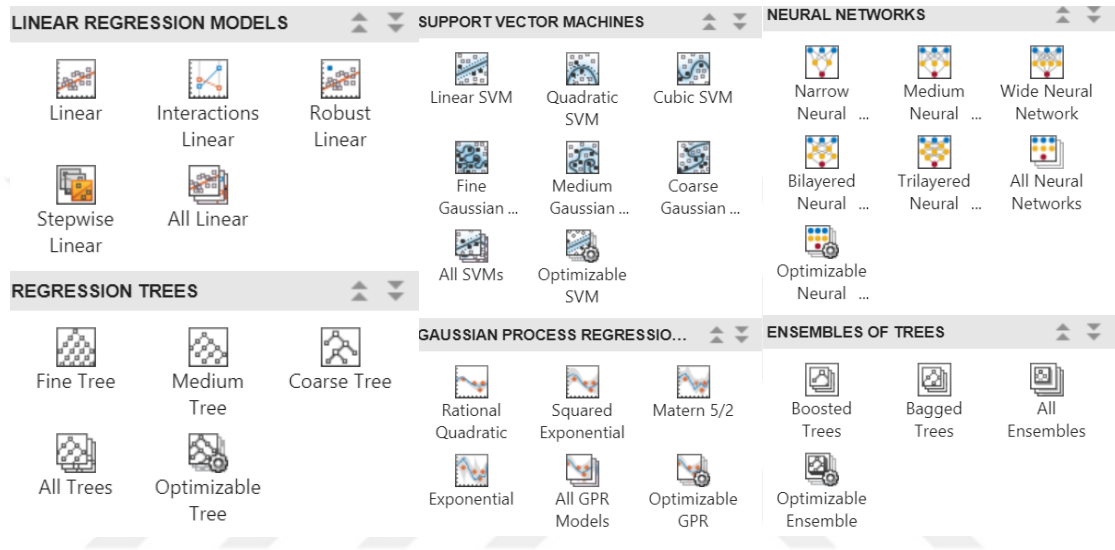


Figure 4.1 MATLAB software regression models

Below is a brief overview of all the modeling techniques used in the study, given in Figure 4.1.

- **Linear regression (LR)**

Linear regression (LR) can be employed to create statistical models that illustrate the relationship between independent variables (explanatory variables) and dependent variables (response variables) [102]. A regression model in which the objective value is anticipated to be a linear combination of the features x_1 to x_n is known as linear regression. In mathematical notation, the predicted value is denoted as y (dependent variable):

$$y(a, x) = a_0 + a_1x_1 + \dots + a_nx_n \quad (4.1)$$

a_0 represents the model's constant, a_i denotes the regression coefficients, which are calculated to minimize the sum of squared deviations, and x_i signifies the independent variables [13].

The following is assumed in linear regression: (i) Existence: The variable y (single variable) is a random variable with a fixed average and variance value in specific probability distributions for a unique combination of independent variables x_i (ii) Independence: The observed values for y are statistically independent and are not correlated with each other. (iii) Linearity of relationships: The average value of variable y is a function that is the linear combination of x_i (iv) Variance homogeneity: The variance of the dependent variable is a constant, as it is obtained through the linear combination of x_i . (e) Normality: The dependent variable is distributed by the linear combination of x_i to achieve normality [102].

- **Regression Trees (RT)**

In a decision tree, each node represents the characteristic or feature evaluated, while the branches proceeding from the node illustrate the evaluation outcome. Regardless of whether it pertains to classification or regression, the class label is assigned to nodes that do not branch, commonly referred to as decision nodes, leaf nodes, or terminal nodes, as illustrated in Figure 4.2. The "root node" represents the highest node in a tree diagram. As a visual and explicit depiction of the decision-making process, decision trees can be helpful when making decisions. Regression as well as classification tasks can benefit from them, with regression trees being tailored to handle continuous data in particular. The dataset undergoes a splitting operation when the root node, which initially contains all of the data, is divided according to the outcomes of the tests. Each succeeding decision node undergoes further testing until the leaf node is finally awarded a value or class. Finding the best way to divide the feature space so that the target variable's variance is minimized inside each division is the objective of the regression tree.

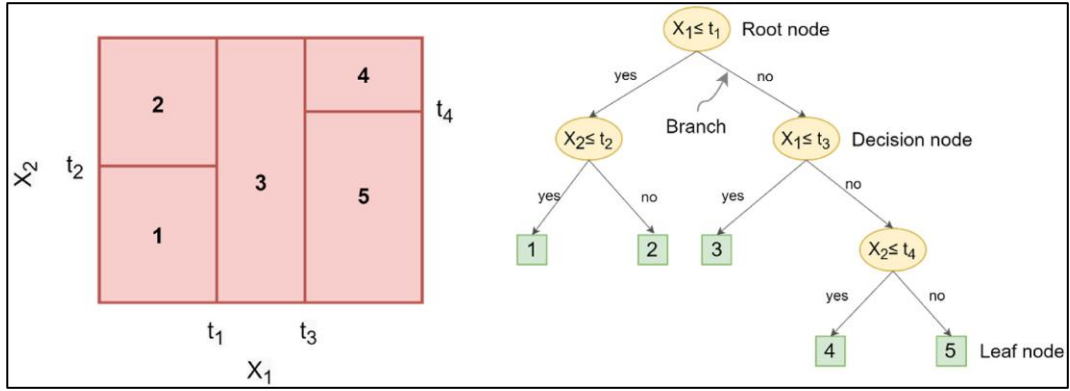


Figure 4.2 An illustration of a regression tree and its corresponding dataset (Source: [103])

Despite their simple tree-like configuration, decision trees can become quite broad and intricate in practice, rendering interpretation relatively challenging. They handle both numerical and categorical data, as well as perform variable screening and feature selection. Machine learning techniques encompass two types of decision trees: regression trees, utilized for continuous outcomes, and classification trees, employed when outcomes can be classified into a finite set of categories. Their amalgamated designation is CART, an acronym for classification and regression trees. In a regression tree, each leaf denotes a numerical value, whereas in a classification tree, the leaves may signify true or false or other categorical outcomes [104].

The advantage of regression trees is that they do not presume linearity in the data, which eliminates the necessity for complex data transformations. This method is more straightforward than linear methods; however, it necessitates careful evaluation to prevent the data from being overfitting. In addition, regression trees implicitly select variables. This implies that a trained regression tree will display more significant variables for predicting the target variable in the tree's earlier nodes. A drawback of simple regression trees is that they are susceptible to model instability. In other words, even minor changes to the dataset may result in a distinct set of partitions, which, in turn, does not result in the most optimally performing model. As a result, more stable ensemble tree models are often used [105].

- **Support Vector Machines (SVM):**

Support vector machine (SVM) is one of the well-known ML methodologies that has attracted considerable attention in literature. Using a support vector machine (SVM) model has many benefits, such as good generalization performance, computational efficiency, high dimensionality resilience, large dimensional object appropriateness, an adaptable application area, and ease of use [106]. The principle of structural risk minimization is implemented by SVM. It generates an optimal separation hyperplane, which is denoted by the formula $w \cdot x + b = 0$. The optimal hyperplane should be determined by minimizing the norm of vectors w :

$$\{x \in S(w, x) + b = 0\} \quad (4.2)$$

Also, as indicated in Equation (4.7), the margin $1/\|w\|$ between the two classes needs to be maximized.

$$\min_{i=1, \dots, n} |(w, x) + b| = 1 \quad (4.3)$$

A linear problem with two classes, each represented by a distinct symbol, is shown in Figure 4.3. The figure shows the support vectors and the margin of utmost separation between the two classes, which are denoted by the dashed squares that encircle the two classes. The margin and those for which $y_i(x_i w) + b$ are constrained by these squares. In other words, the normal vector w of the hyperplane will change if you move any of them [107].

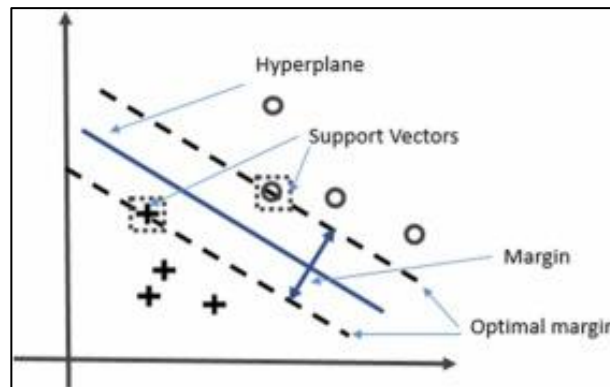


Figure 4.3 SVM fundamental principle and a hyperplane. The ideal hyperplane, which divides the classes, runs parallel to the support vector and lies corresponding bounding hyperplanes (Source: [107])

A mapping function is used by the non-linear SVM to transform the input space's training samples into a higher-dimensional feature space. The SVM model's performance is dictated by its optimal tuning. Three parameters, including the kernel function K , must be optimized. These consist of the kernel parameter (λ), regularization constant (C), and epsilon intensive (ϵ). The kernel function and the parameters applied to the SVM model can significantly affect the accuracy of the model. Various kernel functions, including those listed below, can be used to implement SVM.

$$\text{Radial basis function kernel: } K(x_i, x) = \exp(-\gamma \|x_i - x\|^2) \quad (4.4)$$

where γ is a scaling parameter that determines the influence of each data point.

$$\text{Polynomial kernel: } K(x_i, x) = (\gamma x_i \cdot x + r)^d \quad (4.5)$$

where γ is a scaling parameter r is an offset, and d is the degree of the polynomial.

$$\text{Sigmoid kernel: } K(x_i, x) = \tanh(\gamma x_i \cdot x + C) \quad (4.6)$$

where γ is a scaling parameter, C is an offset, and x_i, x are the training and test patterns, respectively [107, 108].

- **Gaussian Process Regression (GPR):**

After establishing mapping relationships among the items, a Gaussian process regression (GPR) model uses Gaussian regression to represent the data. Deriving the posterior probability distribution in accordance with Bayesian theory, this model first determines the joint distribution of samples. The GPR model, which is based on statistics and is not a parametric regression model, is good at capturing complex and nonlinear interactions, even in high-dimensional space. Its ability to accurately depict complex patterns and behaviors is a key feature, making it a flexible tool with various applications. Fundamentally, GPR is an adaptable approximation of continuous functions in a confined space, contributing to its success in various fields [109].

As an additional non-parametric method, GPR can be expressed for a given input x and output y in the following way:

$$y = h(x)^T \beta + f(x) + \varepsilon$$

$$f(x) \sim N(O, K(x, x'; \theta)) \quad (4.7)$$

where $h(x)$ is a basis function vector that maps the input variables to a multi-dimensional space, β is weighted to the $h(x)$, the function $f(x)$ represents the Gaussian process with mean zero and covariance of $K(x, x')$, in which $K(x, x')$ represents a kernel function, θ is the important parameter that defines the kernel function, and ε is the gaussian noise [110].

- **Artificial Neural Network (ANN):**

Drawing inspiration from the way the human brain processes information, Artificial Neural Networks (ANNs) are among the most popular soft computing approaches. Compared to traditional numerical analysis, ANNs provide more accurate results for complicated problems while using far less computational cost [110]. The human brain quickly recognizes complex non-linear problems. Three simpler layers accelerate calculation. First, gather information through sight or other senses. This information is sent to trained neurons. Activating a trained conglomeration of neurons uses stored algorithms to recognize letter and number shapes in stage three. ANNs use three-layer logic. In the first layer of an ANN, known data is input. The selection of suitable input variables is based on the parameters that need to be predicted. Data from the input layer passes to the hidden layer, which stores algorithms like the human brain. Certain nodes activate depending on network learning from input layer nodes. The amount of information and the level of accuracy of the prediction determine the number of layers of nodes that make up the hidden layer. Finally, the output layer predicts the desired variable using the input variables and the hidden layer with the trained information. The structure of an ANN is represented in Figure 4.4 [111].

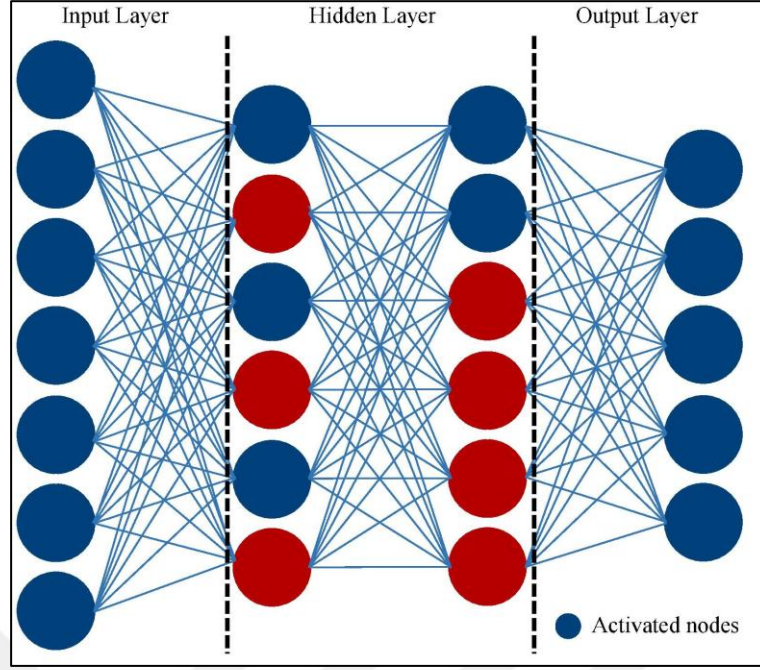


Figure 4.4 Schematic representation of an artificial neural network (ANN) structure consisting of an input layer, two hidden layers, and an output layer (Source: [111])

The mathematical relationship between each hidden node and the input variables can be stated as follows.

$$h_i = \sigma (w_i^T x) \quad (4.8)$$

where x is the vector of p input variables, w_i^T is the weights corresponding to each input variables and the activation function σ is a nonlinear function. The activation function for regression problems is usually a sigmoidal function.

$$\sigma (w_i^T x) = \frac{1}{1+e^{w_i^T x}} \quad (4.9)$$

The hidden nodes h is associated with the predicted output y , as suggested by:

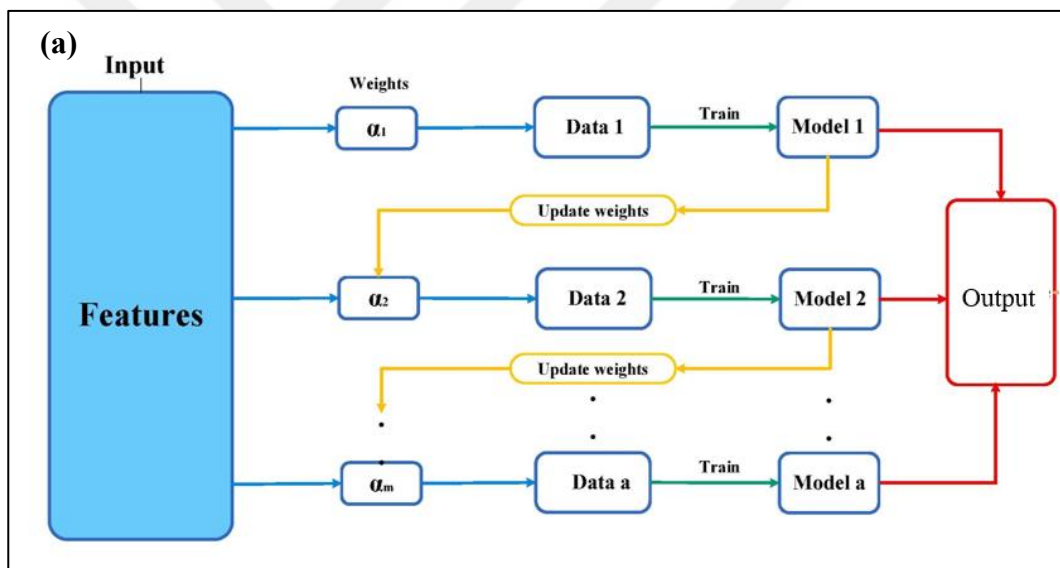
$$y = g (\beta^T h) \quad (4.10)$$

where h is the vector of hidden node values, β^T is defined as another set of weight factors. Although g is capable of being a nonlinear function, it is generally assumed to be the identity matrix, resulting in $y = \beta^T h$ [95].

- **Ensembles of Trees (ET):**

Ensemble learning is a technique that combines a number of different learning algorithms in order to attain superior performance. There are two categories that are used to classify ensemble learning models: boosting and bagging. Through the process of

boosting, a weak learner is obtained by training on the dataset, the outcomes of the training of the weak learner are observed, training samples that are wrong are identified, and an altered training set is used to train the next weak learner. The procedure is continued until a certain number of weak learners, denoted by a , is reached; the weak learners are placed in a weighted group. Bagging, or bootstrap aggregating, is a self-help technique that involves a sampling method with put-back. The training set for each weak learner is divided using random sampling in the bagging process. This results in b sampling sets that are then used to train b weak learners. When the weak learners are added together, the result is a group of strong learners. Examples of boosting methods include adaptive boosting (AdaBoost) and gradient boosting decision trees (such as XGBoost), while random forest serves as an example of a bagging method. The model's structure of boosting and bagging is demonstrated in Figure 4.5 (a) and Figure 4.5 (b), respectively [112].



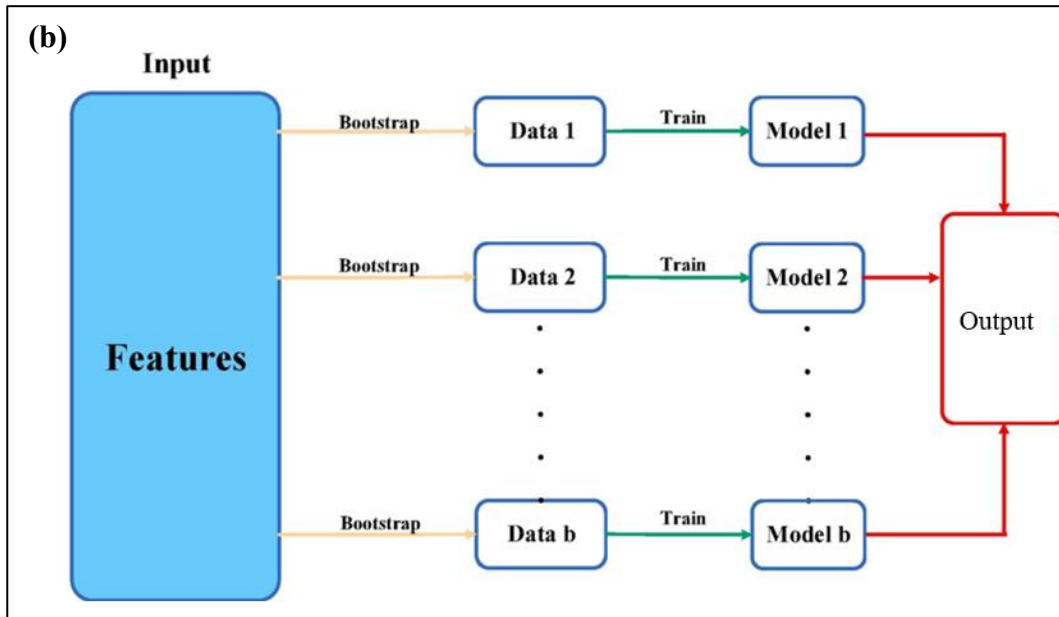


Figure 4.5 Schematic representation of (a) boosting and (b) bagging ensemble models (Source: [112])

4.4.1 Cross-validation

Preventing overfits is a critical issue to consider when training and comparing statistical and machine learning models. ML models trained on datasets that lack a sufficiently large variance of the data (i.e., on datasets that are not rigorously sampled) are susceptible to overfitting, which is an issue for models that are highly capable of learning non-linear relationships. The performance evaluation of the applied machine learning model was conducted using k-fold cross-validation to determine whether the developed machine learning model is sufficiently efficient to predict the outcome of a test dataset [105].

The train-test split, and k-fold cross-validation are the most frequently employed model evaluation methods. The train-test-split approach randomly divides the original dataset into training and testing sets. The model is trained using the training set, and it is subsequently tested using the testing set. Most of the time, two imbalanced datasets are employed as training and testing sets, with a proportion of 80/20 or 70/30. Because these sets are randomly selected, there is a significant possibility that interesting information about the data in the training set will be overlooked when a small dataset is available, which could result in a failure to learn an effective mapping of inputs to outputs. As a result, the predictive model's accuracy would be compromised if a portion of the data were retained for testing. Consequently, this method is not suitable for limited datasets.

The k-fold cross-validation technique is an appropriate solution when a dataset is insufficiently large. In the 20/80 split dataset, the 20-test section was kept separate from the validation test, and validation was applied to only the training sets. The original dataset is randomly divided into k sections (folds) in k-fold cross-validation. It selects a distinct data subset for testing and training the model with the remaining k-1 data subsets in each k-fold of model development and validation. As a cross-validation error, the relevant error is calculated as the meaning of all k-folds. This method offers the benefit of eventual utilization of all dataset data for both training and testing [113].

The 10-fold cross-validation algorithm ($k = 10$) was implemented in this investigation to enhance the model prediction of the ML model through the utilization of a MATLAB program. This was accomplished by employing the inherent MATLAB function "Crossval" with a scalar value of 10. The dataset is arbitrarily divided into ten non-overlapping groups (folds) in the 10-fold cross-validation, as illustrated in Figure 4.6. An equal number of data samples will be present in each fold. The ML model is trained using nine of the ten folds in each of the ten validation rounds (iterations), while the remaining fold is used to assess the ML model. The first fold is employed as the testing set in the initial iteration, while the remaining folds are training the model. The model is tested on the second fold in the second iteration, while the remaining folds are used as the training set. This procedure is repeated until each fold of the 10-folds has been utilized as the testing set.

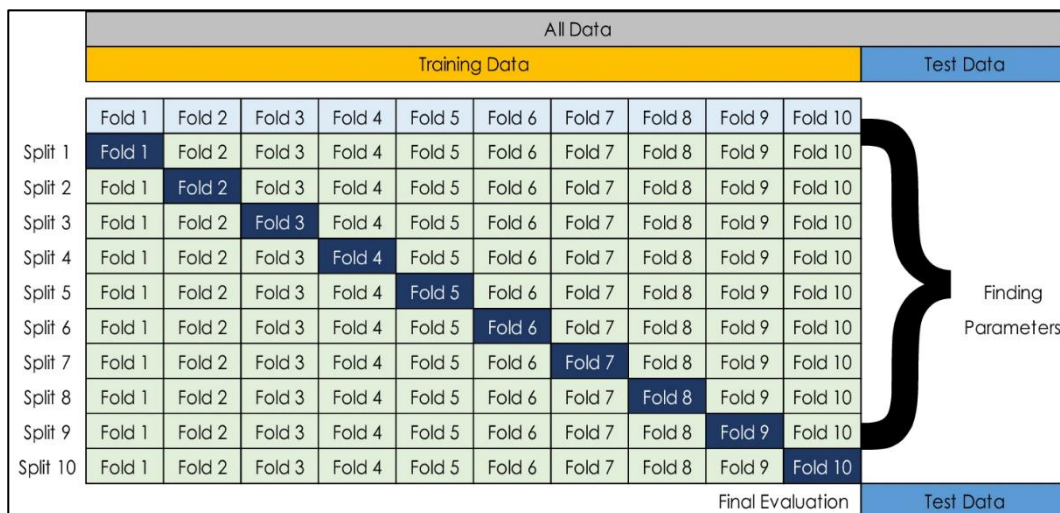


Figure 4.6 10-fold cross-validation (Source: [105])

4.4.2 Hyperparameter configuration method

Hyperparameter configuration is critical for machine learning processes. The model's efficacy and computation time are directly influenced by the selection of hyperparameters. Various hyperparameter tuning techniques, including Grid Search, Random Search, Bayesian Optimization, and Genetic Algorithms, are frequently employed to efficiently search the hyperparameter space and identify the optimal configuration to develop the most effective model [114]. The most frequently applied hyperparameter configuration techniques are grid search (GS) and random search (RS). The schematic diagram of GS and RS is presented in Figure 4.7. After incorporating each parameter combination from the parameter space into the model during training, GS selects the hyperparameter combination with the highest performance. The computational resources and time required for GS increase as the parameter space expands. The computational effort necessary for grid search increases exponentially as the parameter dimension increases. RS constructs a parameter subspace using partial parameter combinations to search within the subspace, ensuring the accuracy of the search while improving the computational performance. This approach does not utilize the entire hyperparameter space. Random search is more effective than grid search for high-dimensional data [115].

The grid search method is the most frequently employed technique for optimizing hyperparameters. It selects the parameter combination that generates the most ideal model performance by iterating through all potential parameter combinations. Nevertheless, the drawbacks of grid search include an efficiency that necessitates an increase when the parameter space is extensive and a running speed that is not optimistic. The principle of random search is identical to that of Grid Search: to randomly test multiple potential combinations of parameters and nearly identify the optimal position, thereby reducing the running time [116]. In this study, random search optimization was used due to the long operating time of the grid search optimization method and the high number of models.

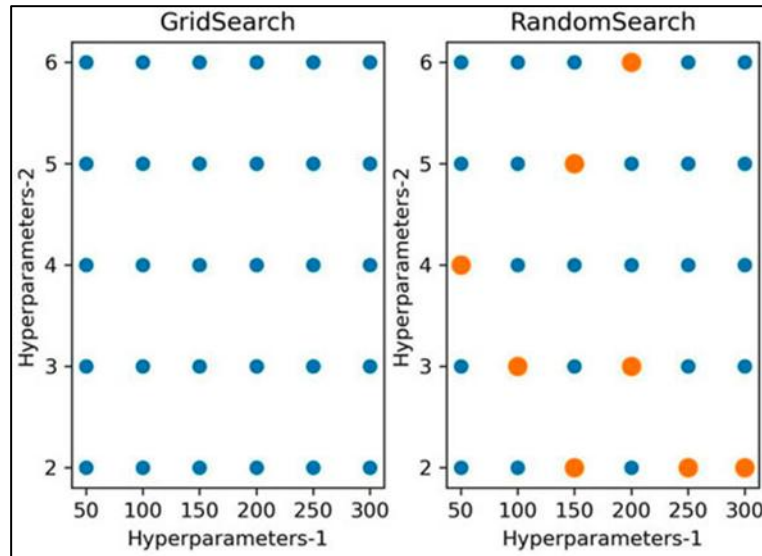


Figure 4.7. Schematic diagram of grid search and random search (Source: [115])

Although hyperparameter optimization is an essential part of model tuning, it was selectively applied in this study only to model types where such optimization was meaningful and applicable. Models such as support vector machines, regression trees, ensemble methods, and Gaussian process regression benefited from systematic grid search strategies to determine their optimal configurations. In contrast, linear regression models, which do not involve tunable hyperparameters in their standard form, were directly trained without any additional optimization step. The methodological integrity of each model type was maintained while computational efforts were distributed effectively thanks to this selective application.

4.4.3 Feature ranking

One of the key steps affecting machine learning models' performance is removing redundant or irrelevant features from the dataset. Therefore, the feature selection process ensures that only parameters containing meaningful information are included in the model, reducing computational burden and increasing accuracy. In regression problems, a mathematical relationship is established between the input parameters and the variable to be predicted, and the strength of this relationship can vary depending on both the initial conditions of the algorithm used and the information in the feature vector. Features are classified according to whether they carry meaningful information about the data; informative ones are considered "relevant," while those containing noise and negatively impacting model performance are considered "irrelevant." While irrelevant features can

negatively impact model performance, relevant features increase predictive power. In this context, feature ranking methods are used to evaluate the contribution of each variable to the model, allowing decisions about which parameters should be retained or eliminated. These techniques preserve the underlying data structure without losing information and improve the model's discriminatory power. As a result, the resulting prediction model is simplified and made more functional by contributing only the influential features [117].

A range of feature ranking techniques—such as Fisher Score, ReliefF, and Information Gain—have been extensively employed in previous studies to evaluate variable importance. One of the methods used for feature selection in MATLAB is the F-test. The F-test, weighted by probability values (P values), examines two hypotheses: null and alternative. Under changing input, the mean values of the output remain the same for the null hypothesis, while the mean values of the output are not the same for the alternative hypothesis [118].

In this study, feature ranking analysis was conducted to examine the relative effects of input variables on the predicted outputs. The F-test method was used to determine the statistical significance of each feature. This approach offered valuable insights into the model's sensitivity to different input variables, enabling clear visualization and interpretation of their relative influence.

4.5. Model Evaluation Metrics

Evaluating models' accuracy level and generalization ability is one of the most critical steps in developing machine learning models. Performance evaluation is carried out to determine the extent to which the developed models can make reliable and accurate predictions. This evaluation allows the success levels of different algorithms on the same dataset to be compared and the most appropriate model to be selected. In addition, it is understood during this process whether the model has problems such as overfitting or underfitting.

Three different performance indicators were used when evaluating the test results of the models. These three indicators are the coefficient of determination (R^2), Root Mean Square Error (RMSE), and Mean Absolute Error (MAE). Theoretically, the lower the RMSE and MAE, the more accurate the evaluation. The R^2 value ranges from 0 to 1. When the values obtained for R^2 are close to 1, the model's predictive capacity is proved.

R^2 represents the proportion of the variance in the dependent variable from the independent variables. It is defined as,

$$R^2 = 1 - \frac{\sum_{i=1}^n (y_i - y'_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2} \quad (4.11)$$

where y'_i is the predicted value, y_i is the actual y_i value, $\bar{y}$ is the averaged actual value, and n is the number of observations.

RMSE is the square root of the mean of the square of all of the error. It is defined as,

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (y_i - y'_i)^2} \quad (4.12)$$

MAE is the average of the absolute value of the error, which is very commonly used to measure the accuracy of predicted values. It is defined as,

$$MAE = \frac{1}{n} \sum_{i=1}^n |y_i - y'_i| \quad (4.13)$$

4.6. Development and Calculation of the Multi-Criteria Compatibility Index (MCCI)

In blended cementitious systems containing SCM, the interaction with superplasticizers plays a decisive role, particularly in the hydration processes and compressive strength development. The nature of this interaction can vary significantly depending on the system components and environmental conditions, necessitating multifaceted and holistic approaches for reliable performance assessment. These multifaceted interactions can vary significantly depending on variables such as the chemical and physical properties of the PC, the type of SCM, and the type of superplasticizer. While various studies in literature have attempted to assess this compatibility, analyses have mostly focused on a single performance criteria (e.g., flowability, hydration rate, or compressive strength, as detailed in Table 2.6). These approaches present challenges in assessing the overall system behavior and do not allow for a comprehensive assessment of compatibility.

The Multi-Criteria Compatibility Index (MCCI), developed within the scope of this thesis, integrates multiple performance parameters to express the overall compatibility of

Portland cement-SCM-superplasticizer systems with a numerical and comparable score. The MCCI method normalizes parameters with different scales and units to a common evaluation basis and then calculates the overall compatibility score by relating these parameters to predetermined weighting coefficients. This allows diverse and interdisciplinary parameters such as hydration kinetics (e.g., onset time, onset heat, induction period, total heat), thermogravimetric analysis (e.g., Ca(OH)_2 content), and compressive strength to be included in the same evaluation system.

MCCI's unique contribution to literature is not only its integration of multiple criteria but also the ability to flexibly assign weights to each parameter based on the system's needs. This feature allows the index to be adapted to different application areas or project priorities. For example, while early-age strength is prioritized in prefabricated structural elements, late-age strength or long-term durability parameters may be prioritized in infrastructure applications. Such prioritizations enable the index to be used effectively in application-based decision-making processes. The MCCI approach, which goes beyond analyses based on single criteria such as flowability, zeta potential, and adsorption capacity, commonly used in the literature (shown in table 2.6), enables holistic system evaluation and provides systematic and quantified tool for formulation optimization and PC, SCM or SP type selection. In this respect, MCCI provides both a strong methodological basis for academic research and serves as a practical decision-making mechanism in cementitious systems.

In this study, the MCCI quantitatively assesses compliance through the weighted contributions of key hydration kinetic parameters, CH content, and compressive strength results at different ages. This multi-criteria assessment system provides an objective criterion for selecting suitable superplasticizer types for different SCMs and provides a methodological basis for future research in this area. The index enables standardized evaluation and comparison where complex interactions between multiple variables must be considered simultaneously. In this regard, the performance parameters considered in the MCCI calculation, the weights assigned to each, the evaluation direction (positive/negative) and the technical evaluation justifications of each parameter are summarized in Table 4.3. These parameters were selected to describe the key aspects of hydration behavior, thermal analysis, and compressive strength development relevant to superplasticized blended cement systems. Each parameter contributes to the MCCI index based on its relative importance and influence on compatibility. The weighting system

reflects the relative importance of each parameter to overall performance. Negative weights indicate parameters where lower values are preferable (e.g., onset time, induction period), while positive weights denote parameters where higher values are beneficial (e.g., total heat at 72 hours, compressive strength). In this way, each weight reflects both the relative importance and the evaluation direction of the parameter.

To ensure that all parameters could be evaluated on the same scale, regardless of their original units or ranges, each value was normalized to fall within a 0 to 1 interval. Depending on whether higher or lower values indicated better performance, one of two equations was used. Equation 4.14 was applied to parameters where higher values are desirable, while Equation 4.15 was used for those where lower values are more favorable.

$$N_i = (x_i - x_{\min}) / (x_{\max} - x_{\min}) \quad (4.14)$$

$$N_i = (x_{\max} - x_i) / (x_{\max} - x_{\min}) \quad (4.15)$$

Where N_i is the normalized value, x_i is the original measured value, and $x_{\min}$ and $x_{\max}$ are the minimum and maximum values observed for that parameter across the feasible synthetic mixtures after applying the filtering criteria.

The final compatibility score is calculated as the weighted sum of these normalized parameters using Equation 4.16:

$$MCCI = \sum (w_i \times N_i) \quad (4.16)$$

Where w_i represents the weight assigned to parameter i , and N_i represents the normalized value of parameter i . Higher scores indicate better overall compatibility between the PC-SCM-SP system.

Table 4.3 MCCI parameters with their weights, evaluation criteria, and description

Parameter	Weight (%)	Evaluation	Description
Onset time (min)	5	Negative	Longer onset times indicate delayed hydration beginning
Onset heat (mW/g cement)	5	Positive	The intensity of the initial hydration reaction, indicating early reactivity potential of the binder system
Induction period (min)	10	Negative	Duration of minimal hydration after initial wetting; affected by the interaction between the superplasticizer and SCM, with shorter periods indicating better early-age compatibility
Total heat at 72 h (J/g cement)	10	Positive	Correlates with the overall degree of hydration and strength development
Relative CH content at 3 days (%)	10	Negative	Indicates early hydration progress and pozzolanic activity potential
Relative CH content at 28 days (%)	10	Negative	Reflecting the extent of CH consumption through pozzolanic and the long-term binder reactivity
Compressive strength at 2 days (MPa)	15	Positive	Critical for early demolding and rapid construction needs; particularly important in blended cement systems where early strength development is often limited due to slower reaction kinetics
Compressive strength at 7 days (MPa)	15	Positive	Indicates the intermediate strength development of the cementitious system
Compressive strength at 28 days (MPa)	15	Positive	Standard reference age for cementitious system strength evaluation
Compressive strength at 90 days (MPa)	5	Positive	Represents long-term strength development, particularly relevant for blended cement systems where pozzolanic or latent hydraulic reactions contribute significantly to the evolution of mechanical performance over time.

In this study, a data-driven approach was adopted to analyze MCCI calculations across a broader formulation space, rather than limiting the calculation to experimental data. In the first step, a synthetic (randomly generated) mixture dataset of approximately 5000 rows was generated using MATLAB software, comprising various combinations of PC content, water/binder ratios, superplasticizer dosages, and other mixture parameters. To ensure that the models remained within their domain of validity, synthetic mixtures were generated within the common experimental ranges of the training datasets. The limits were primarily constrained by the compressive-strength dataset which had the narrowest range. The variable ranges used in creating the synthetic dataset were determined from the overlapping domains of the experimental data, with the compressive strength dataset providing the narrowest limits. These limits were selected because the regression models had been trained within these intervals, and predictions are therefore expected to be more reliable within this domain of validity. During dataset generation, the parameter values were sampled from a uniform distribution across each defined range, ensuring that no region of the formulation space was disproportionately overrepresented. Synthetic mixtures were generated within the following parameter ranges: OPC content 45–90% (by mass of binder); SP dosage 0.00–1.54% (by mass of binder); SCM d_{10} 0.7–1.9 μm ; SCM d_{50} 4.0–10.8 μm ; CaO content 0.2–37.7%; w/b ratio 0.40–0.50; and $\text{SiO}_2 + \text{Al}_2\text{O}_3$ 48.8–90.8 %. Although OPC content 100% was also present in the experimental program, it was excluded from the synthetic dataset to avoid biasing the results toward Portland cement systems. The focus of this study was on blended cement systems with higher SCM content; therefore, mixtures containing 100% OPC were excluded, since they would have shifted the results unfairly toward higher compressive strength values. In addition, the four superplasticizer types employed in the experimental program (PNS, PMS, PCE, and LHA) were included in the synthetic dataset generation.

In the second step, machine learning models were trained on previously obtained experimental data with various regression algorithms (e.g., Neural network, Gaussian Process Regression, etc.). The accuracy of these models was evaluated using classical performance metrics (e.g., R^2 , RMSE, and MAE), and the model with the highest predictive performance was selected. Using this model, ten different parameters included in the MCCI index, shown in Table 4.3, were predicted for the 5000 synthetic mixtures generated. This process is consistent with the approach described in the literature as high-throughput virtual screening (HTVS), which allows for the virtual evaluation and pre-

selection of a large number of potential systems without experimentation. HTVS refers to screening strategies developed to rapidly and systematically select materials that meet target properties from large candidate space. Because the use of high-fidelity models alone incurs significant computational costs, multi-stage HTVS systems typically balance the computational load by sequentially integrating models with varying levels of accuracy and cost. In these approaches, low-fidelity models narrow the pool by eliminating low-probability candidates in the initial stages, while more complex, high-fidelity models are run only on potential candidates. HTVS is widely applied in fields such as biology, chemistry, and materials science, particularly in targeted material discovery and formulation development processes [119, 120].

In this context, using a randomly generated synthetic dataset containing 5000 different mixtures, MCCI parameters (shown in Table 4.3) were estimated for each mixture by regression models. The obtained prediction results were evaluated within the scope of physical validity and internal consistency criteria before proceeding with the MCCI calculations. In particular, it was stipulated that compressive strength values follow the strength development order ($2 \text{ days} < 7 \text{ days} < 28 \text{ days} < 90 \text{ days}$), and mixtures that did not meet these criteria were eliminated. Furthermore, physically impossible negative values were also revealed in the regression predictions of hydration kinetics. Because such results were unrealistic, they were considered outside reasonable limits, and the relevant mixtures were removed from the data set. At the end of this multi-stage elimination process, 1602 of the initial 5000 mixtures were found to be consistent; MCCI values were calculated for these mixtures alone, creating the final data set.

4.7. Summary of the Computational Workflow

The overall computational process employed in this study consisted of several systematic steps designed to support the development and evaluation of machine learning-based regression models. First, experimental datasets obtained from isothermal calorimetry (310 samples), thermal analysis (217 samples), and compressive strength (144 samples) tests were independently structured and preprocessed. This involved data splitting, feature selection based on correlation analysis, and categorical variable encoding. In contrast to conventional practice, normalization was not implemented, as preliminary trials indicated that the model's performance was diminished when

normalization was implemented. This decline in performance is believed to be the result of the model's inability to distinguish significant but minor differences, which was exacerbated by the narrowing of the data distribution following normalization, as the original data had remarkably similar values.

Following data preparation, a total of 29 regression models across six algorithm families were trained using MATLAB's Regression Learner toolbox. During model development, 10-fold cross-validation was employed to ensure generalizability and reduce overfitting risk. Hyperparameter optimization was performed using systematic random search strategies. Still, it was applied only to model types where tuning parameters were available, such as support vector machines, regression trees, and ensemble methods.

Each regression model class was evaluated to determine the three with the highest prediction accuracy. The results were detailed after selecting the best model from these three classes. Only the most successful models were reported to concentrate on the study and facilitate the comparison of model trends for readers. These selected models were then used to generate the regression outputs necessary for developing the Multi-Criteria Compatibility Index (MCCI), which constitutes the essential contribution of this thesis. The entire computational workflow is summarized in the flowchart presented in Figure 4.8.

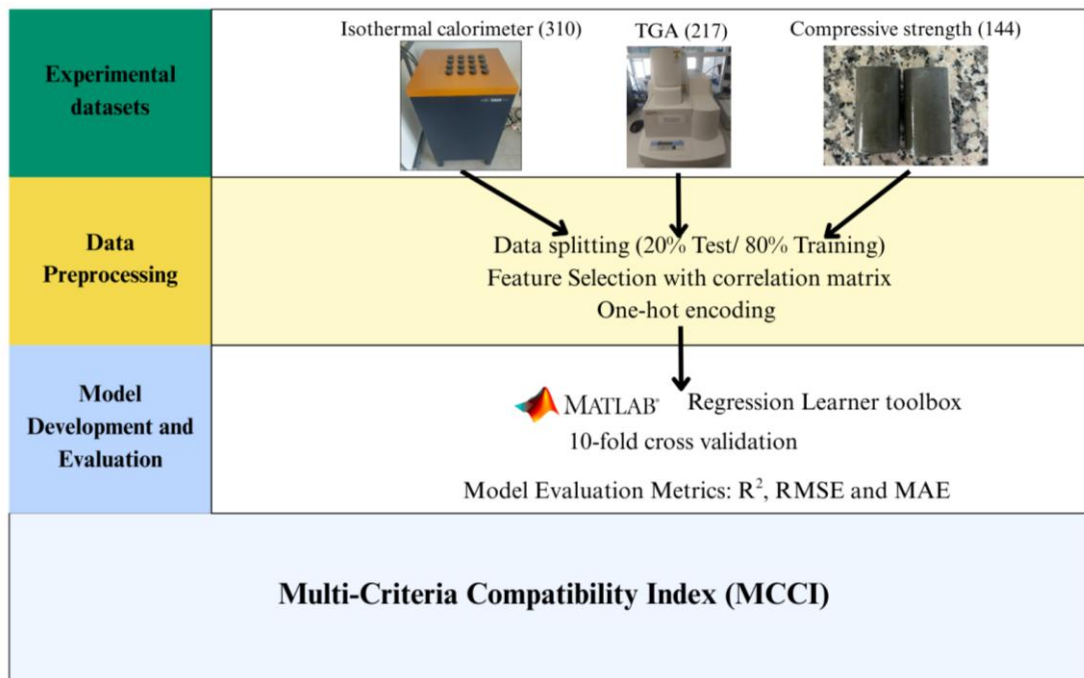


Figure 4.8. Flowchart of the computational workflow

Chapter 5

Results and Discussion

5.1 Influence of Superplasticized Blended Cementitious Systems on Hydration Kinetics

In cementitious systems, hydration initiates with the chemical interaction of the components, and the heat released during this process offers significant insights into the system's reactivity. It is crucial to analyze the hydration kinetics when SCM and SP are incorporated into the system, as the hydration kinetics depend on the component interactions and the type of additive used. In this section, the rate of heat evolution and total heat of hydration obtained by isothermal calorimetry were evaluated.

In this study, a variable prioritization-based correlation matrix was used to reduce the complexity of comparing numerous experimental parameters while evaluating hydration kinetics in 310 superplasticized blended cement samples. The correlation matrix enables the comparative evaluation of parametric effect degrees by revealing the degree and direction of linear relationships between independent and dependent variables in such multivariate systems. A correlation matrix is an assessment of the relationship between two variables. Regression values range from -1 to $+1$, indicating the relationship. A value of -1 between two variables signifies a negative linear relationship, whereas 0 denotes the absence of a relationship between the specified variables. A $+1$ indicates a positive correlation between two variables [121]. Especially since there are many physical and chemical parameters used experimentally in this study, the correlation matrix allows the determination of factors that significantly affect the hydration kinetic parameters by distinguishing variables with ineffective or limited effects. In this respect, the correlation matrix is not only a preliminary analysis tool but also a methodological filtering mechanism that allows the results to be interpreted with a technically consistent approach.

The correlation matrix, which quantitatively shows the linear relationships between the input variables and the four outputs demonstrating the hydration kinetics (onset heat, onset time, induction period, and total heat at 72 h), is presented in Figure 5.1. As a result of the statistical analysis carried out through the correlation matrix, OPC content (in other words SCM replacement level), SCM $\text{SiO}_2+\text{Al}_2\text{O}_3$ and CaO ratios (briefly SCM oxide composition and therefore SCM type) and superplasticizer content, which exhibit significant linear relationships with four main hydration outputs, were determined as the main inputs affecting the hydration kinetics of the superplasticized blend cementitious system. At this point, although SP content was determined as one of the main inputs affecting hydration kinetics, it should be noted that this variable is not independent of the water/binder ratio (w/b ratio) in this study. Because the superplasticizer dosages used in the study were not determined randomly, they were determined by a mini-slump test to provide equivalent flowability at different w/b ratios and binder compositions. In other words, the amount of SP required to reach the targeted mini-slump value for each w/b ratio was determined, and the experimental design was shaped accordingly. This situation partially limits the independence assumption between SP content and w/b ratio variables in the correlation matrix. It shows that especially the evaluation of these two variables together should be done carefully in the interpretations.

Focusing on these three inputs (OPC content or SCM replacement level, SCM type and SP content due to w/b ratio) in the evaluation of isothermal calorimeter experimental results was aimed both to increase technical consistency and to avoid redundancy and complexity that can be created by comparing multiple variables. This strategic decision enables a more systematic and comparable analysis of hydration kinetics. Although 310 isothermal calorimeter experiments were conducted in this study, only a limited number of experiments selected according to specific criteria were analyzed in detail within the scope of the thesis. The main reason for this is that evaluating all experiments one by one would create a voluminous and complex structure that would exceed the scope of the study. In addition, since the primary focus of this thesis is to develop a compatibility index using machine learning techniques in line with the data obtained, a detailed comparative evaluation of all experiments will not directly serve the research question of this thesis. Therefore, only representative examples will allow meaningful comparisons in terms of basic inputs such as SCM replacement level, SCM type, and SP content, depending on the w/b ratio, are presented.

	OPC content	PNS	PMS	PCE	LHA	SP content	SCM d ₅₀	w/b ratio	SCM SiO ₂ +Al ₂ O ₃	SCM CaO	Onset heat/ Onset time/Induction period/Total heat at 72h
OPC content	1.00										
PNS	-0.06	1.00									
PMS	-0.07	-0.32	1.00								
PCE	-0.10	-0.33	-0.33	1.00							
LHA	0.03	-0.30	-0.30	-0.31	1.00						
SP content	-0.25	0.06	0.10	-0.31	0.28	1.00					
SCM d ₅₀	-0.05	0.04	0.03	0.02	0.06	-0.24	1.00				
w/b ratio	-0.09	0.00	0.01	-0.02	0.02	-0.16	-0.03	1.00			
SCM SiO ₂ +Al ₂ O ₃	-0.17	0.08	0.08	0.08	0.07	0.51	0.08	-0.25	1.00		
SCM CaO	-0.20	0.02	0.01	0.00	0.03	-0.55	0.33	0.26	-0.61	1.00	
Onset heat	-0.38	0.03	0.09	0.16	-0.21	0.39	0.08	-0.10	0.44	-0.49	1.00
Onset time	-0.12	0.00	-0.02	-0.05	0.12	0.16	-0.27	-0.25	0.39	-0.25	1.00
Induction period	-0.16	-0.01	0.03	-0.11	0.17	0.26	-0.31	-0.28	0.45	-0.30	1.00
Total heat at 72 hours	-0.58	0.06	0.26	0.14	-0.33	0.19	0.11	0.25	0.18	0.01	1.00

Figure 5.1 Correlation matrix plot between inputs and hydration kinetics outputs

5.1.1 Influence of SCM replacement level

Plot of hydration rate and cumulative heat of hydration shown in Figure 5.2, Figure 5.3 and Figure 5.4 were selected to evaluate the effect of different replacement level (20–55%) on blended cement (BC) hydration kinetics in systems containing natural pozzolan ground for 120 minute (NP_120min), blast furnace slag (BFS) and calcined clay1 (CC1), respectively. All measurements were conducted with an isothermal calorimeter at 25 °C for 72 hours. The sample shown as PC1_control in all graphs represents the blank control sample prepared at 0.45 water/cement ratio and containing without SCM or SP. The same Portland cement (PC1) and constant water/binder ratio ($w/b = 0.45$) were used in all blended cement mixtures. Additionally, PNS was used as the superplasticizer type in all blended cement mixtures. SP dosages were not constant as per the principle of the study. Instead, they were adjusted according to the equivalent dosage principle to obtain a similar mini-slump in each system. This approach allows the effect of the SCM replacement level alone to be evaluated in isolation, considering the characteristic water requirements of mixtures with different replacement levels. These selected results are presented as highly representative examples from a wide range of experimental data and provide a preliminary assessment for the main objective of the study, which is the development of the compatibility index.

The heat flow curve observed during the typical hydration process of Portland cement is shown in Figure 5.2. The effect of SCM replacement and/or superplasticizer admixtures on the phases of this curve is of critical importance. The first prominent peak is associated with the formation of hydration products of the silicate phases; the increase in heat released here is attributable to the increase in the solubility of C_3S . After this initial period of strong reaction, a slowdown is observed in the system. During this phase, a second heat release peak occurs, corresponding to the rapid formation of ettringite and the increase in C_3A dissolution at the point where sulfate is reduced. This second peak is referred to as the sulfate depletion point. The third peak occurs in the next phase due to the hydration of the remaining aluminates in the system. Isothermal calorimeter curves of control cement paste (PC1) and blended cement pastes containing different replacement levels of natural pozzolan ground for 120 minutes (NP_120min) are given in Figure 5.2. According to the hydration rate curves, higher peaks are observed in both blended cement

systems compared to the control sample without SCMs. The significant increase observed in the silicate peak (peak I) can be attributed to the increase in the early age reaction rate of the cement and is associated with the filling effect of natural pozzolan. Similar effects of SCM on the rate of hydration have been reported in the literature, especially during this early peak. These effects are related to the SCMs acting as fillers and the formation of nucleation surfaces that accelerate the precipitation of hydration products and promote the hydration of clinker phases [122]. When the sulfate depletion point (peak II) is evaluated, there appears to be no significant change compared to the control sample or as the replacement level increases.

Blended cement pastes containing natural pozzolan, a slight increase in the height of the aluminate peak (peak III) is observed when compared to the PC1 control sample. This suggests the system is insufficient in sulfate, and the aluminate phases react rapidly and uncontrollably. The total amount of calcium sulfate in the cement mass decreases as the SCM substitution increases, while the clinker ratio remains constant. This may lead to insufficient sulfate amounts, especially those required to balance the hydration of the aluminate phases. Also, the filling effect of SCM may accelerate the hydration of aluminate phases and increase early-age heat release [123]. Although the NP used in the study is not as high as metakaolin or calcined clay, the fact that it contains approximately 7% Al_2O_3 may support sulfate consumption by increasing the formation of ettringite. This may have caused a higher aluminate peak formation, especially in the mixture containing 40% NP. These findings indicate that the optimum sulfate content in cements blended with NP should be re-evaluated.

When the cumulative heat of hydration plot is evaluated, the blended cement pastes release higher total heat than the control sample. Especially, the mixture with a 40% replacement level reaches the highest total hydration heat, indicating that the filling effect of SCM becomes apparent. This effect increases the nucleation areas by providing more reaction surfaces for cement hydration and thus indirectly accelerates the hydration process. This increase, which started from the first 24 hours, continued steadily until 72 hours and revealed the direct proportional relationship between the increase in replacement level and the cumulative heat of hydration.

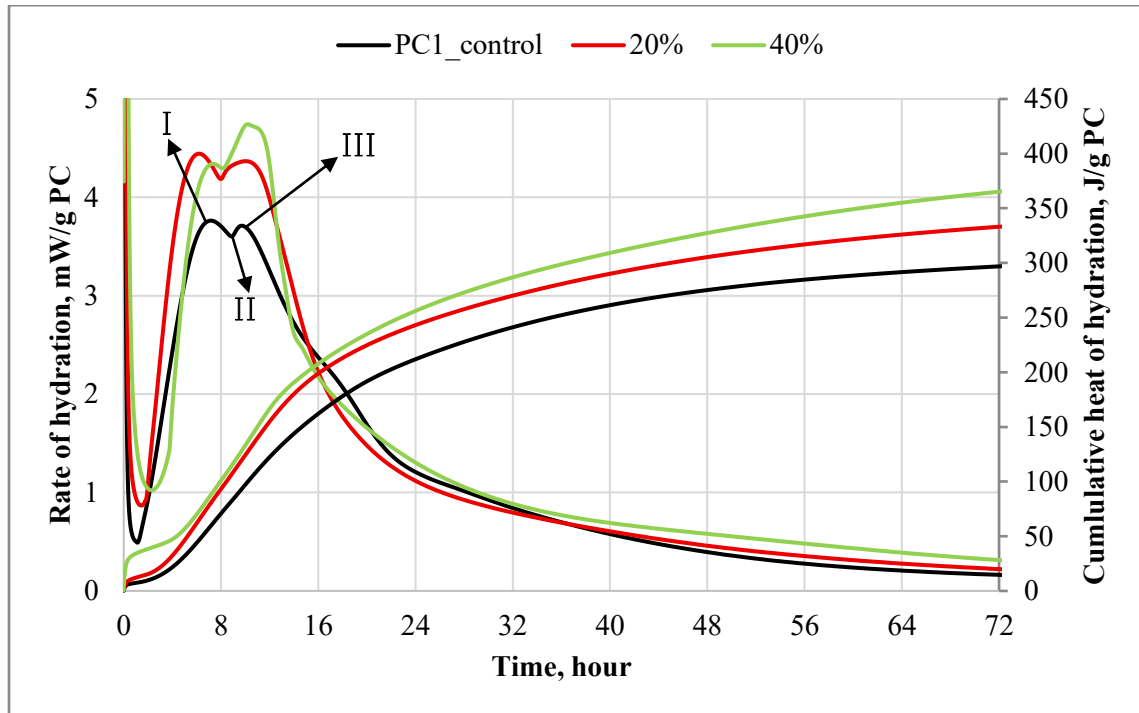


Figure 5.2 Isothermal calorimetry results for PC1 and NP_120min blended cement pastes

Isothermal calorimeter curves of control cement paste (PC1) and blended cement pastes containing different replacement levels of blast furnace slag (BFS) are given in Figure 5.3. The silicate peak (peak I) represents the dissolution process of C_3S phase and the formation of $Ca(OH)_2$ with C-S-H. As the BFS substitution rate increases (especially at 55%), this peak appears both higher and at an earlier time. This is related to the physical effects of the slag, which are the filling and the nucleation effect due to its high surface area, thus accelerating the early-age silicate hydration. Also, according to Schöler et al., the water-cement ratio (w/c) increases due to SCM, which initially shows minimal reaction. This additional water increases the amount of Portland cement that reacts after 1 day and beyond, providing more water and more space for hydrates to grow [38]. Therefore, the increase in the silicate peak at 55% substitution level compared to other mixtures can be attributed to the formation of more voids as the substitution rate increases and the faster precipitation of hydrates into these voids. The second peak, the sulfate depletion peak, is related to the formation of ettringite and the dissolution of C_3A . While no meaningful change occurs in this peak as the substitution rate increases, there are significant differences in the third peak, the aluminate peak. At high substitution levels, the sulfate balance disruption occurs more rapidly, which causes more aggressive hydration of the aluminate phases. In addition, this situation is also related to the late

reactivity of the slag and the fact that it contains a certain amount of alumina [38]. The reason for the broadening of the aluminate peak is that, as sulfate is depleted, aluminate hydration slows down and spreads over time under sulfate deficiency conditions. As long as sulfate is in solution, aluminate quickly forms ettringite to complete the reaction. Still, if sulfate is depleted, aluminate dissolution and hydration continue at a slow rate, so the reaction does not end suddenly but rather extends, causing the peak to broaden [124]. This effect becomes significant at a 55% substitution rate, indicating that the sulfate addition in the mixture should be adjusted.

The total heat of hydration shows the energy released per gram of PC. In other words, even if the amount of PC in the blended cement mixture decreases as the BFS substitution rate increases, the remaining cement releases more heat. Especially at a 55% substitution rate, the total heat released per PC has increased significantly. In the literature, the increase in reactivity per gram of PC is explained by two different mechanisms. First, the reaction of slag with water releases heat. Second, the filling effect, which is also mentioned in natural pozzolans, increases the water/cement ratio and the increase in nucleation areas, increasing the clinker hydration at an early age [125].

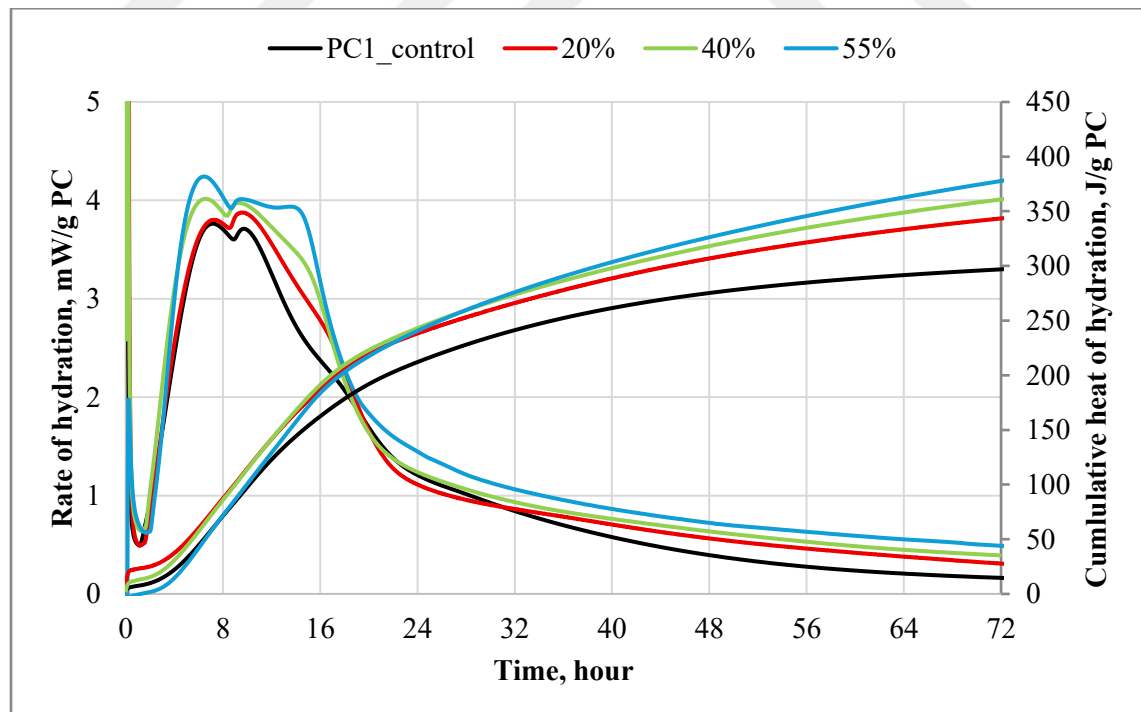


Figure 5.3 Isothermal calorimetry results for PC1 and BFS blended cement pastes

Isothermal calorimeter curves of control cement paste (PC1) and blended cement pastes containing different replacement levels of calcined clay 1 (CC1) are given in Figure 5.4. The effect of CC1 on the cement hydration process has a significant impact on both early and late age reactions. As the substitution rate increases, the decrease in Ca^{2+} and alkalinity levels in the system due to clinker dilution limits the rate of initiation of hydration reactions. However, the physical filling and nucleation effect of calcined clay plays an accelerating role by promoting C-S-H nucleation at early ages [52]. These two effects affect early hydration behavior complexly, depending on the replacement level. Especially at high replacement levels (40%), a reaction profile is observed that starts with a sudden and high hydration rate in the first hours but decreases rapidly in a short time. This situation is interpreted as a characteristic complexity that occurs as a result of the combination of the nucleation effect formed by the acceleration of dissolution of the increased specific surface area in the system, the insufficiency of reactive clinker phases, and the rapid absorption of water by calcined clay, reducing free water. Therefore, depending on the substitution rate, early-age hydration behavior shows both acceleration and deceleration trends, causing a complex effect.

According to Py et al., the amount of sulfate in limestone calcined clay (LC3) systems is critical for the balanced progress of the hydration process. When the sulfate content is insufficient, sulfate depletion occurs early, and alite reactions can be suppressed due to uncontrolled hydration of aluminate phases, which negatively influence strength and hydration kinetics. When the sulfate content is increased to optimum levels, the sulfate balance is achieved, the hydration of alite and aluminate phases proceeds in a balanced manner, and maximum performance is obtained from the system. If the sulfate content is excessive, the sulfate remains in the environment for a long time, the hydration process can be prolonged, and durability problems such as delayed ettringite formation (DEF) can occur. Therefore, careful optimization of the sulfate content in LC3 designs is necessary for both early age and long-term performance [126]. In Figure 5.4, sulfate depletion behavior is observed with a more pronounced and high intensity peak in the control mixture, the fact that the sulfate amount remains constant despite the alumina contained in the calcined clay disrupts the sulfate-aluminate balance and changes the sulfate requirements. This situation reduces the intensity of aluminate hydration reactions under sulfate control during the transition from the ettringite formation phase to the monosulfate phase. It causes these reactions to occur later with the increase in the

replacement level. In Figure 5.4, it is seen that the peak due to aluminate hydration shifts to the right, and its intensity decreases as the replacement level increases.

Regarding cumulative heat of hydration, the cement pastes blended with calcined clay initially exhibited lower heat release than the control sample. Still, this difference diminished over time and ultimately surpassed the control. A noticeable increase in the late-stage hydration rate was observed, especially at 30% and 40% substitution levels. The reason for this can be attributed to the fact that calcined clay activates pozzolanic reactions by increasing the consumption of $\text{Ca}(\text{OH})_2$ due to its high specific surface area and amorphous structure at later ages, and increases the reactivity of the system at later ages by supporting the formation of secondary C-S-H and aluminate hydrate. As a result, calcined clay substitution significantly affected both the early-age hydration kinetics and the late-age hydration properties.

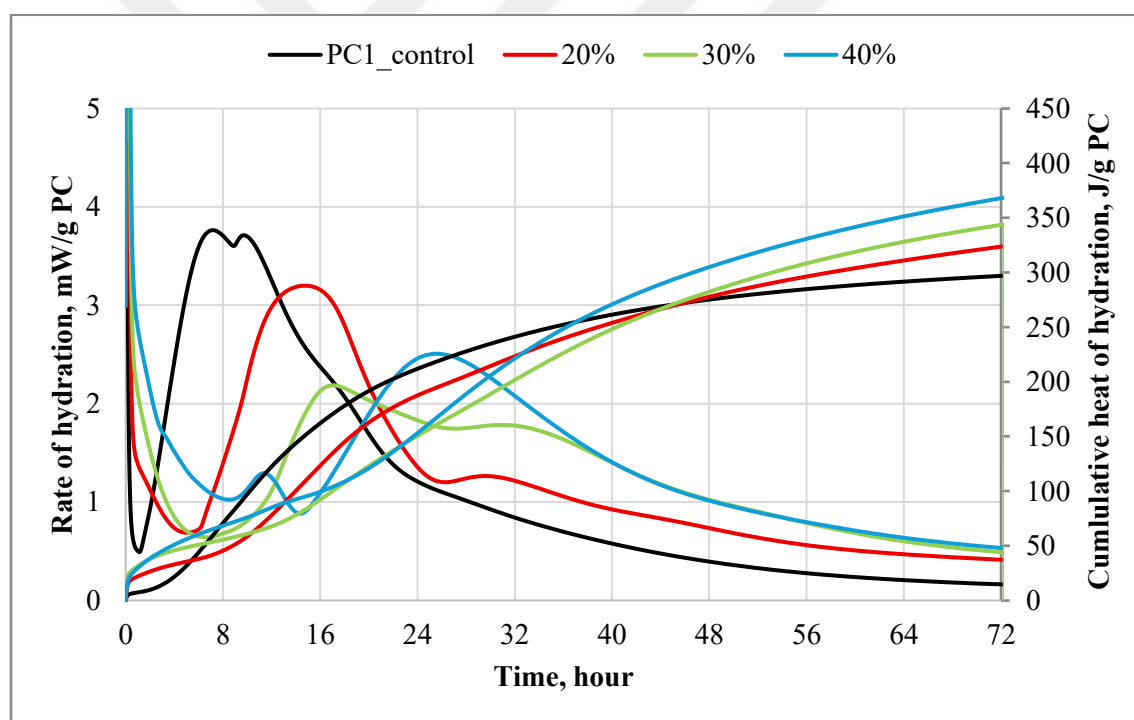


Figure 5.4 Isothermal calorimetry results for PC1 and CC1 blended cement pastes

5.1.2 Influence of SCM type

SCMs initially show inert behavior in cementitious systems, but later they can affect the properties of cementitious systems by participating in hydration reactions. SCMs show different pozzolanic properties depending on their type, fineness, mineralogical, and chemical composition. This has various effects on the hydration kinetics of blended

cements [127]. Isothermal calorimeter curves of control cement paste (PC1) and blended cement pastes with various SCMs at 20% and 40% replacement levels are given in Figure 5.5 and Figure 5.6, respectively. The sample shown as PC1_control in all graphs represents the blank control sample prepared at 0.45 water/cement ratio and containing without SCM or SP. The same Portland cement (PC1) and constant water/binder ratio ($w/b = 0.45$) were used in all blended cement mixtures. Additionally, PNS was used as the superplasticizer type in all blended cement mixtures. SP dosages were not constant as per the principle of the study. Instead, they were adjusted according to the equivalent dosage principle to obtain a similar mini-slump in each system.

In this study, the effects of different SCM types on cement hydration were evaluated in terms of their chemical compositions and grain size distribution. While the particle size distribution of SCMs directly affects the initiation time and rate of reactions during the hydration process and shapes the hydration kinetics of the system, SCM chemical composition determines the reaction potential and continuity. Finer particles of SCMs can accelerate the formation of hydration products at an early age by providing a heterogeneous nucleation surface; however, agglomeration, which can be seen in extremely fine particles, can limit this effect. On the other hand, SCMs with high silicate and aluminate content contribute to the development of hydration by providing free ions after dissolution and supporting secondary C-S-H gel formation with pozzolanic reactions at later ages. Therefore, the effects of SCMs on the hydration process are not limited to their chemical compositions alone, but they form a multidimensional interaction that should be evaluated together with their particle size, solubility, and mineralogy [128].

The silicate peak is particularly related to the dissolution of the C_3S phase and the formation of the primary C-S-H gel. Blended cement pastes with BFS are of medium fineness ($d_{50} = 10.8 \mu m$) and show latent hydraulic properties in the presence of alkalis and $Ca(OH)_2$ due to their high CaO (37.7%) and reactive SiO_2 content, and clearly show the silicate peak. Natural pozzolan, especially when ground for 120 minutes ($d_{50} = 5.2 \mu m$), accelerates the C_3S dissolution by creating a nucleation effect with its fine structure and makes the silicate peak more distinct, but due to its high SiO_2 (71.2%) and low CaO content, the peak does not increase in size as much as BFS. CC1 ($d_{50} = 4 \mu m$) accelerates the silicate peak by providing early-age resolution with its high fineness, but its long-term reactivity remains limited due to its low CaO content. The CC2 does not have a significant accelerating effect on the silicate peak due to its very coarse grain ($d_{50} = 20 \mu m$), but

contributes to the hydration process in the later hours with its high SiO_2 and Al_2O_3 content. As seen in Figure 5.4, the sulfate depletion point varies significantly depending on the type of SCM used. In the control sample (PC1_control) and BFS blended cement pastes, the sulfate depletion point occurred at approximately 10–11 hours. In natural pozzolan and CC2, the sulfate depletion point was observed earlier hours (around 7 hours). Silva et al. reported that since the use of high limestone and calcined clay in LC3 systems dilutes the clinker, the high Al ion release of calcined clay and the filling effect of limestone accelerate hydration, increase sulfate consumption, and complicate the formation of ettringite and AFm. This situation causes the aluminate peak after the silicate peak in isothermal calorimetry to be delayed and broadened, and the apparent sulfate depletion point in OPC cannot be observed in LC3-like systems. In addition, the increased $\text{Al}_2\text{O}_3/\text{SO}_3$ ratio in LC3 supports early AFm formation and spreads sulfate consumption over a wide range [129]. A similar effect is observed for CC1, and the sulfate depletion point cannot be observed as in other blended cements. Other SCMs continued the sulfate consumption at a level close to the control cement, thus not significantly slowing down the hydration rate. This behavior of SCMs has a direct effect on the hydration kinetics of the system and is important in terms of setting time, early strength development, and ettringite formation control. It has been observed that SCMs, such as CC1 in particular, can control the hydration rate by delaying sulfate depletion and significantly changing the hydration behavior. The aluminate peak is formed by the rapid reaction of aluminate phases after the depletion of sulfates and is the second important acceleration stage of the hydration process. No significant differences were observed in other blended cement mixtures except CC1.

Regarding cumulative heats of hydration, BFS provides the highest heat release at both early and late ages with its high CaO and reactive SiO_2 content, contributing to the formation of a continuous binder phase in the cement matrix. Despite its medium fineness, it provides long-term heat increase thanks to its latent hydraulic structure. NP, especially in the finely ground ($d_{50} = 5.2 \mu\text{m}$), accelerates early hydration due to the filling effect and consumes Ca(OH)_2 by pozzolanic reactions, contributes to the formation of secondary C-S-H gel in the long term, so it increases the cumulative heat, but this increase does not reach values as high as BFS. It is observed that the cumulative heat of hydration of CC1 is low in the first hours (0–48 hours), but increases rapidly in the following hours and almost catches up with other blended cements and even surpasses natural pozzolan at

72 hours. This situation can be explained by the activation of pozzolanic reactions that support the formation of secondary C-S-H and aluminate hydrate by consuming $\text{Ca}(\text{OH})_2$ over time, despite the low heat release due to the limited reaction of CC1 at the beginning.

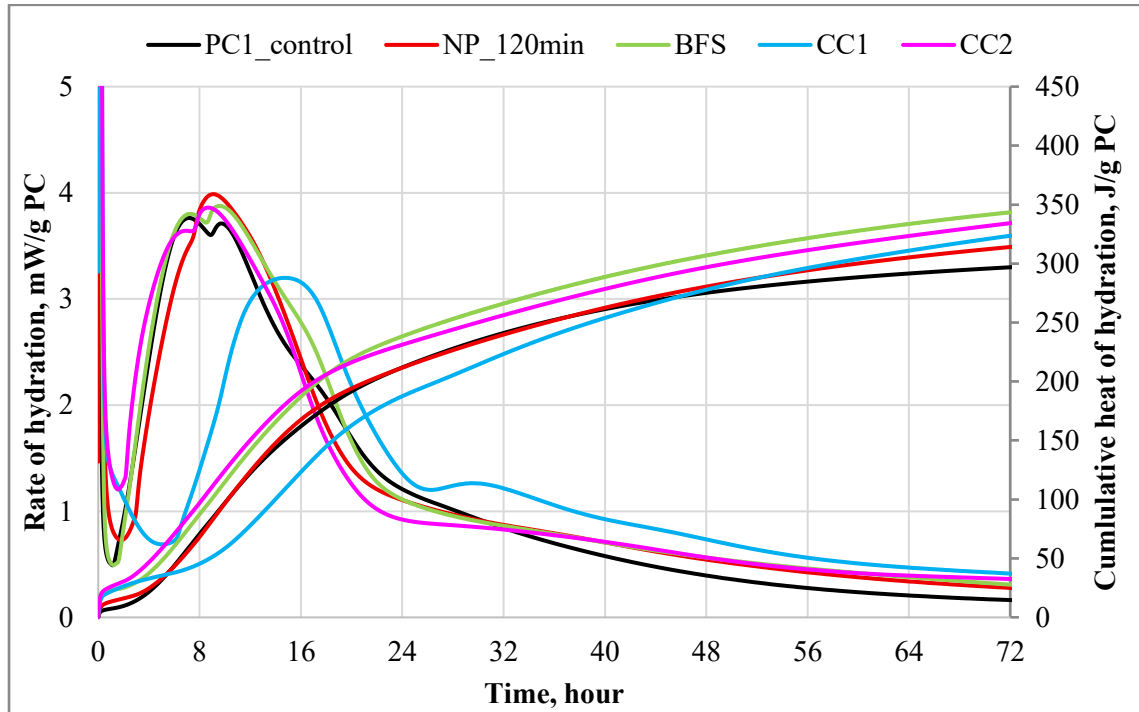


Figure 5.5 Isothermal calorimetry results for blended cements with various SCMs at 20% replacement level

As shown in Figure 5.6, SCM types can have different effects at increasing replacement levels. The increase in the natural pozzolan replacement level resulted in higher cumulative heat release. This can be attributed to the increased filler effect. However, a shift to the right was observed in the hydration rate graph due to the increased SP requirement. Although BFS releases heat due to its hydraulic properties, this effect could not overcome the filling effect of natural pozzolan after the first hours. CC1 accelerates the hydration rate initially due to the increased specific surface area and physical filling-nucleation effect at early ages. However, the rate decreases quickly due to the decrease in free Ca^{2+} and rapid absorption of water due to clinker dilution. Especially at high substitution rates (40%), a complex hydration profile is formed that starts rapidly but decreases in a short time. At late hours, CC1 increases calcium hydroxide consumption result of pozzolanic reaction and supports secondary C-S-H formation and increases the hydration rate above the control mixture after 38 hours. As a result, CC1 exhibits complex hydration kinetics, especially with high replacement levels.

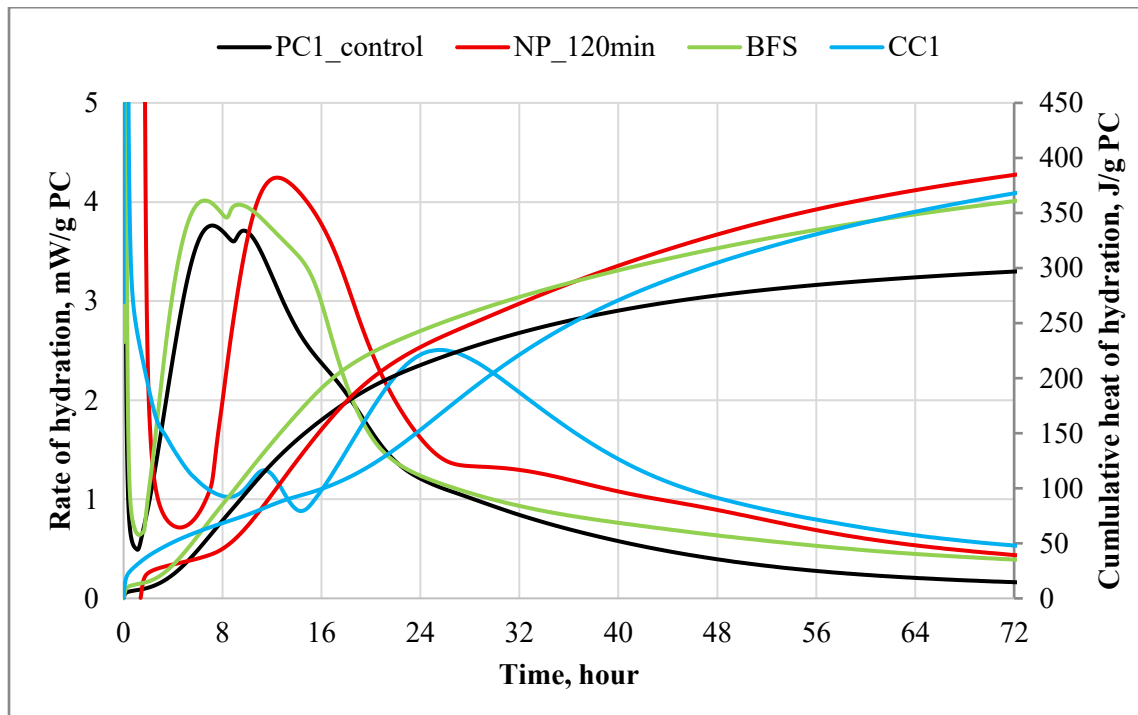


Figure 5.6 Isothermal calorimetry results for blended cements with various SCMs at 40% replacement level

5.1.3 Influence of SP content or w/b ratio

In cementitious systems, the water/binder (w/b) ratio is one of the key parameters that directly affect the hydration kinetics. Especially when SCMs are included in the system, it complicates the behavior. At low w/b ratios, although a high heat of hydration is released initially, the hydration rate decreases in a short time due to the limited void and water amount. On the other hand, at high w/b ratios, the void increases, more space is generated to develop hydration products, and higher hydration degrees can be achieved in the long term. Since the pozzolanic reactions of SCMs and cement hydration proceed simultaneously, the w/b ratio plays a critical role in determining the interaction and progress rate of these two reactions. Therefore, determining the appropriate w/b ratio stands out as one of the most important parameters affecting the performance of blended cement systems in terms of both strength and durability [130, 131].

Isothermal calorimeter curves of control cement paste (PC1) and 120 min grinding natural pozzolan blended cement (BC) pastes with PNS and LHA at varying w/b ratios are given in Figure 5.7 and Figure 5.8, respectively. As shown in Figure 5.7, increasing the water/binder (w/b) ratio decreases the hydration heat release rate at early ages but

increases the cumulative heat of hydration in the long term. Blended cement pastes at a low w/b ratio (0.45) reach a slightly higher hydration rate with a higher silicate peak, and this peak occurs earlier. This is due to the rapid formation of reaction products due to the low void volume. On the other hand, at high w/b ratios (0.55), the peak hydration rate is lower but occurs slightly later, and the increasing amount of water in the system expands the void volume around the binder particles, providing more space for the development of hydration products and supporting the progress of the reaction. Control pastes (PC1) exhibit lower hydration rates than blended cement (BC) pastes at early hours, while BC mixtures accelerate hydration by reaching higher peak values, especially at early hours. However, in the long term, the cumulative heat of hydration of BC mixtures reaches higher levels than control pastes, and this is associated with the pozzolanic reactions, secondary C-S-H formation, and the increase in reactivity of the system with the filler effect provided by SCMs. The filler effect accelerates the hydration of binder phases at early ages by promoting the nucleation of hydration products on the surface of SCMs, and this effect supports both early and late age performance of the system with pozzolanic reactions.

Figure 5.8 illustrates that using LHA in blended cement mixtures leads to significant differences in the effect of w/b ratio on hydration kinetics compared to the mixtures with PNS shown in Figure 5.7. LHA usage delays the hydration process by causing the hydration rate to occur at lower levels at early ages and peaks to form later. However, with the increase in w/b ratio, the cumulative hydration heat increase trend is maintained in the long term. BC mixtures reach a higher total hydration heat compared to control pastes. This situation shows that despite the LHA, the reactivity of the system continues to increase in the long term due to the filler effect provided by SCMs and the pozzolanic reactions. As a result, while LHA suppresses the hydration rate in the early hours compared to PNS, it contributes to the continuation of the hydration process of the system and the increase in reactivity at later ages, with the effect of SCMs at late hours.

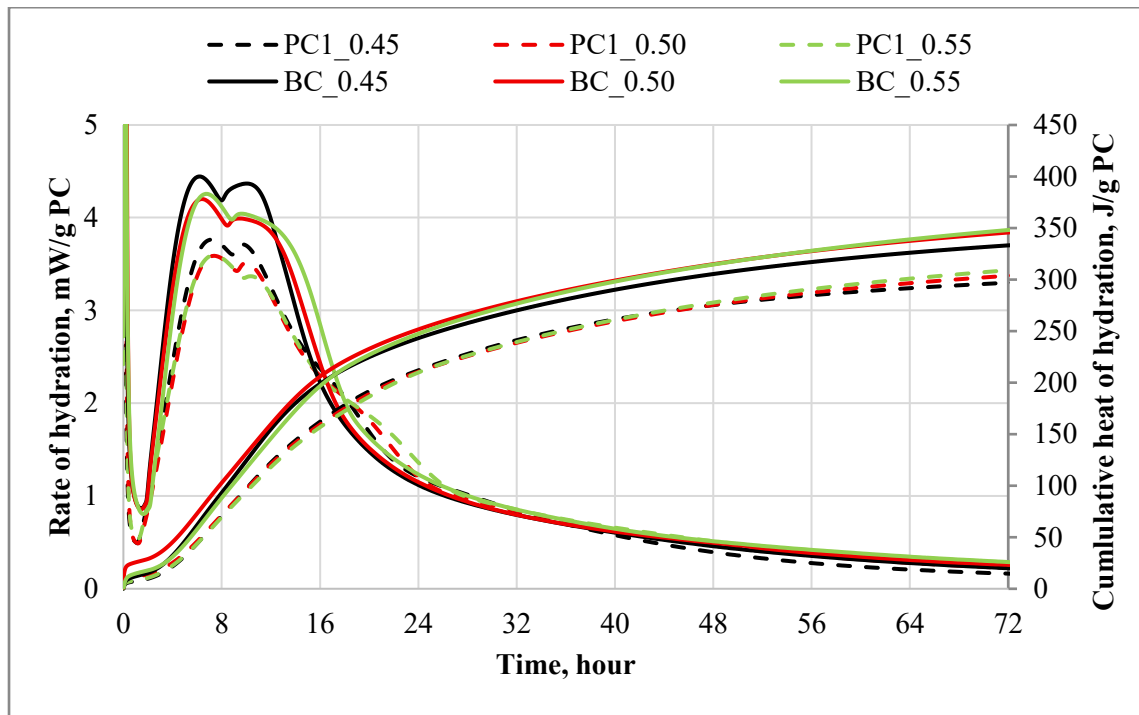


Figure 5.7 Isothermal calorimetry results for PC1 control and NP_120 min blended cement (BC) pastes with PNS at varying w/b ratios

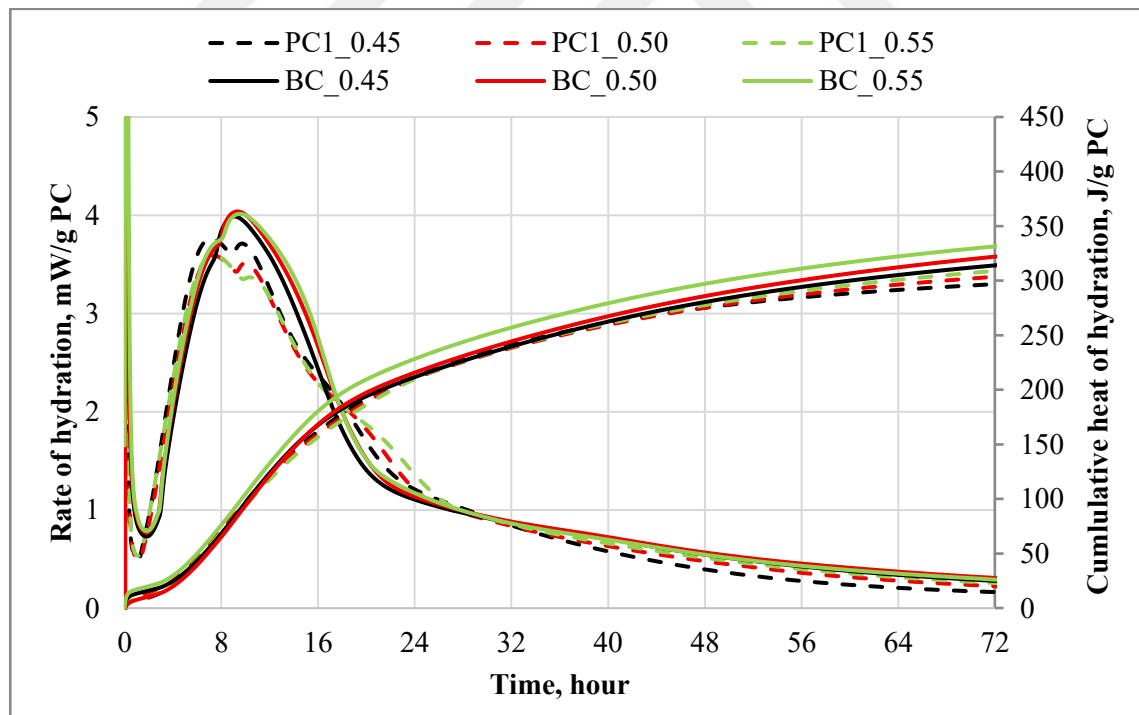


Figure 5.8 Isothermal calorimetry results for PC1 control and NP_120 min blended cement (BC) pastes with LHA at varying w/b ratios

5.2 Influence of Superplasticized Blended Cementitious Systems on CH Content

SCMs play a significant role in increasing the strength and durability of cementitious systems by reacting with calcium hydroxide (CH) to form C–S–H gel. In the literature, this property is defined as pozzolanic behavior. CH reacts with C–S–H gel to form additional C–S–H gels, thus contributing to the filling of large capillary pores and reducing the porosity of the system, increasing its strength and impermeability. In addition, since both the amount and size of CH crystals decrease during the pozzolanic reaction process, particle size refinement is achieved, which contributes to both matrix and interfacial transition zone densification. In addition, since high CH content may negatively affect durability in aggressive environmental conditions, the determination of CH consumption is critical for durability design and long-term performance prediction of systems containing SCM [132-134]. Different methods are used to determine pozzolanic activity, including thermal analysis, X-ray diffraction, chemical titration, Chapelle test, Frattini test, saturated lime solution test, electrical conductivity measurement, and isothermal calorimetry. These methods provide the opportunity to evaluate the pozzolanic properties of SCMs from different perspectives by following the decrease in the amount of CH, changes in the ion concentration in the solution, increase in strength, differences in electrical conductivity, or heat release during the reaction [135]. In this study, the amount of portlandite (CH) was determined in 217 different cements and blended cement pastes using the TGA method. Thus, the pozzolanic activities of the SCMs used were evaluated in detail under the effect of different parameters (w/b ratio, SP type, SP content, age, etc.).

Measuring pozzolanic activity by determining CH consumption in blended cement pastes containing SCM with thermal analysis methods is a widely used method. Thermal analysis methods include thermogravimetric analysis (TGA) and/or differential thermal analysis (DTA). According to Juenger and Siddique, some important points to consider when using these methods are as follows [8]:

- The decomposition temperature of CH is not constant in all samples.

The decomposition temperature varies depending on factors such as the amount of alkali in the system and the particle size. Therefore, examining the DTA graph to determine the

appropriate temperature for each sample is important in correctly calculating the CH amount.

- Drying the samples causes evaporative water loss.

Since the pastes are stored mainly by drying before the TGA test, the loss of evaporative water affects the measurement results. Since the amount of evaporative water varies depending on the hydration degree of the sample and the water/cement ratio, differences may occur in the mass loss calculations. To prevent this situation, the samples can be tested without drying, the evaporative water loss can be included in the calculations, or using an “ignited weight” as the sample weight.

- Exposure of the samples to carbon dioxide causes calcium carbonate formation.

Calcium carbonate formed due to CO₂ exposure during grinding, drying, storage, and testing should be considered in the measurements and included in the calculations by comparing it with the value in the original cement.

- Other hydration products also lose mass in the CH decomposition temperature range.

The mass loss of other hydration products in the decomposition temperature range of CH may lead to an overestimation of the CH amount in the measurements. Therefore, it is recommended to use modified calculation methods to eliminate this error.

In this study, various precautions were taken to minimize the errors that may be encountered in the measurements. First of all, the CH decomposition temperature was determined separately for each paste using the DTA curve, thus preventing temperature-related measurement errors. In order to prevent evaporative water loss in the samples, without drying, the samples were tested, and the ignited weight was taken as the basis for the calculations. To minimize calcium carbonate formation due to CO₂ exposure, the samples were stored in airtight syringes immediately after preparation. At the testing time, the syringes were carefully opened under controlled conditions, and the samples were promptly grounded and subjected to analysis to ensure minimal atmospheric interaction before measurement. In addition, after the CH decomposition temperature was determined, the amount of other hydration products decomposed in the same range was calculated based on the slope value obtained at the point immediately before this temperature on the TGA curve and deducted from the total CH amount, thus ensuring high accuracy in measurements. Further details regarding the CH content calculation methodology can be found in Section 3.3.3.

In this study, the large number of input variables and 217 samples analyzed by thermal analysis make direct comparison challenging. Therefore, a correlation matrix approach based on variable prioritization was adopted. Thus, linear relationships between independent variables in the system and CH content at 3 and 28 days, which are the thermal analysis outputs, were systematically analyzed. The correlation matrix serves as a methodological filtering tool that allows determining and interpreting which variables significantly affect CH content by distinguishing the degrees of influence of inputs in multivariate systems. The correlation matrix, which quantitatively shows the linear relationships between the input variables and the two outputs demonstrating the thermal analysis (CH content at 3 day and 28 day), is presented in Figure 5.9. As a result of the statistical analysis performed on the correlation matrix, the superplasticizer content, SCM $\text{SiO}_2 + \text{Al}_2\text{O}_3$ and CaO ratios (in short, SCM oxide composition and therefore SCM type) and OPC content (in other words, SCM replacement level), which showed significant linear relationships with the CH content measured at both ages, were determined as the main inputs affecting the CH consumption of superplasticized blended cementitious systems. At this point, although SP content was determined as one of the main inputs affecting CH consumption, it should be noted that this variable is not independent of the w/b ratio in this study. The superplasticizer dosages used in the study were not determined randomly; on the contrary, they were optimized with mini slump tests to provide equivalent fluidity at different w/b ratios and binder compositions. In other words, the amount of SP required to reach the targeted mini-slump value for each w/b ratio was determined, and the experimental design was shaped accordingly. This situation partially limits the assumption of independence between the SP content and w/b ratio variables in the correlation matrix. It shows that interpretations should be made with caution, especially when evaluating these two variables together.

In the evaluation of CH contents performed by the TGA method, in order to maintain consistency of the analyses and to prevent confusion that may occur in multivariate comparisons, the focus was on basic inputs such as OPC content (or SCM replacement level), SCM type, and SP content determined depending on the w/b ratio. Although CH measurements were made on a total of 217 samples in this study, only representative and comparable samples were analyzed in detail within the scope of the thesis. This approach allows the systematic evaluation and interpretation of the main parameters affecting CH consumption in line with the main objective of the research.

	OPC content	PNS	PMS	PCE	LHA	SP content	SCM d ₅₀	w/b ratio	SCM SiO ₂ +Al ₂ O ₃	SCM CaO	3-day/ 28-day
OPC content	1.00										
PNS	-0.10	1.00									
PMS	-0.02	-0.37	1.00								
PCE	-0.02	-0.37	-0.36	1.00							
LHA	0.16	-0.31	-0.29	-0.29	1.00						
SP content	-0.22	0.03	0.11	-0.34	0.23	1.00					
SCM d ₅₀	0.01	-0.01	-0.01	-0.01	0.02	-0.28	1.00				
w/b ratio	-0.18	0.04	0.04	0.04	-0.12	-0.06	-0.24	1.00			
SCM SiO ₂ +Al ₂ O ₃	0.36	-0.06	-0.01	-0.01	0.09	0.45	-0.08	-0.43	1.00		
SCM CaO	-0.33	0.05	0.01	0.01	-0.07	-0.58	0.20	0.25	-0.95	1.00	
3-day	0.13	0.10	-0.34	0.10	0.15	-0.76	0.19	0.12	-0.55	0.64	1.00
28-day	0.52	-0.01	-0.21	0.03	0.21	-0.75	0.20	-0.11	-0.28	0.40	1.00

Figure 5.9 Correlation matrix plot between inputs and 3-day and 28-day relative CH content outputs

5.2.1 Influence of SCM replacement level

The Ca(OH)_2 (CH) contents of the control cement paste (PC1_control) and blended cement pastes at 3 and 28 days of age, along with the CH values normalized to the Portland cement ratio and the calculated relative CH contents, are presented in Table 5.1. The numbers at the end of the names indicate the replacement level in the blended cement in the mixture notations used in this table. For example, the expression “BFS40” indicates that 40% blast furnace slag (BFS) is substituted in the mixture. Normalized CH content allows fair comparison of the pozzolanic reactivity of mixtures with different SCM replacement levels. Blended cement pastes were prepared by replacing natural pozzolan (NP), blast furnace slag (BFS) and calcined clay1 (CC1) with Portland cement at different replacement levels; experiments were conducted at rates of 20% and 40% for NP, 20%, 40% and 55% for BFS, and 20% and 30% for CC1. PC1 type Portland cement was used in all cement pastes in this table, and all mixtures were prepared at a water/binder ratio of 0.45. Additionally, PNS was used as the superplasticizer type in all blended cement mixtures. SP dosages were not constant as per the principle of the study, but instead were adjusted according to the equivalent dosage principle in order to obtain a similar mini slump in each system. This approach allows the effect of the SCM replacement level alone to be evaluated in isolation, considering the characteristic water requirements of mixtures with different replacement levels. After the determined curing periods were completed, the samples were analyzed by thermogravimetric analysis (TGA) method, and their Ca(OH)_2 contents were determined. These selected results are presented as highly representative examples from a wide range of experimental data and provide a preliminary assessment for the main objective of the study, which is the development of the compatibility index.

According to the normalized CH contents given in Table 5.1, it is seen that the CH values at the end of 3 and 28 days in the control mixture are 14.7% and 15.2%, respectively. This increase is an expected result due to the hydration of the Portland cement. In the hardened blended cement pastes with NP, the normalized CH contents were measured as 11.6% and 8.8% at 20% replacement level in 3 and 28 days, while these values decreased to 8.7% and 0% at 40% replacement level. This situation shows that as the NP replacement level increases, CH consumption increases due to the pozzolanic

reaction, and CH is even completely consumed, and this effect becomes more apparent with hydration age.

In the hardened blended cement pastes with BFS, the normalized CH contents corresponding to 20%, 40% and 55% replacement levels were measured as 14.6%, 14.7% and 13.1%, respectively, in 3 days, and 11.8%, 10.5% and 8.2% at the end of 28 days. These data show that BFS keeps CH content at levels close to the control mixture at an early age, but decreases CH content at later ages due to the effect of pozzolanic reaction. In addition, it was observed that the decrease in 28-day CH values became more pronounced as the replacement level increased.

In the hardened blended cement pastes with CC1, while the normalized CH contents in the mixture with 20% replacement level were 12.4% and 11.3% at the end of 3 and 28 days, these values were determined as 12.0% and 7.3% in the mixture with 30% replacement level. The results show that CC1 keeps CH content at lower levels at an early age compared to the control mixture, and at later ages, it increases CH consumption depending on the replacement level, leading to a decrease in CH content.

In general, it is revealed that the normalized CH content in the control Portland cement paste slightly increases, while in the cement pastes with SCMs, a decrease occurs with the consumption of CH due to pozzolanic reactions with hydration age. As the SCM replacement increased, more significant decreases were observed in the normalized CH content at both 3 and 28 days, which was associated with the increase in the pozzolanic reactivity of the SCMs and the increase in CH consumption in the system. The decrease in the amount of CH in blended cement pastes is due to the production of less CH in the mixture due to SCM replacement and the consumption of the CH formed by pozzolanic reactions [136]. Similarly, Vance et al. observed a tendency for decreasing normalized CH contents with increasing the replacement level of metakaolin and limestone and hydration age, which was explained by the dilution effect depending on the replacement level and the pozzolanic reactivity of the SCMs. It was concluded that especially the highly reactive additives, such as metakaolin, change the composition and amount of hydration products by consuming the CH amount formed in the system, thus, CH content is not only an indicator of the degree of hydration but also a parameter that can be used to evaluate the pozzolanic activity of SCMs [137].

Table 5.1 CH contents of control and blended cement pastes with different replacement levels at 3 and 28 days

Cement type	CH content (%)		Normalized CH content (%)		Relative CH content (%)	
	3 days	28 days	3 days	28 days	3 days	28 days
PC1_control	14.7	15.2	14.7	15.2	100.0	100.0
NP20_120min	9.3	7.0	11.6	8.8	78.9	57.9
NP40_120min	5.2	0.0	8.7	0.0	59.2	0.0
BFS20	11.7	9.4	14.6	11.8	99.3	77.6
BFS40	8.8	6.3	14.7	10.5	100.0	69.1
BFS55	5.9	3.7	13.1	8.2	89.1	53.9
CC120	9.9	9.0	12.4	11.3	84.4	74.3
CC130	8.4	5.1	12.0	7.3	81.6	48.0

5.2.2 Influence of SCM type

The CH contents of the control cement paste (PC2_control) and blended cement pastes with different SCM types at 3 and 28 days of age, along with the CH values normalized to the Portland cement ratio and the calculated relative CH contents, are presented in Table 5.2. PC2 type Portland cement was used in all cement pastes in this table, and all mixtures were prepared at a water/binder ratio of 0.45. Additionally, PNS was used as the superplasticizer type in all blended cement mixtures. SP dosages were not constant as per the principle of the study, but instead were adjusted according to the equivalent dosage principle to obtain a similar mini slump in each system. This approach allows the effect of the SCM replacement level alone to be evaluated in isolation, considering the characteristic water requirements of mixtures with different replacement levels.

The normalized CH contents presented in Table 5.2 clearly reveal the effects of different SCM types on pozzolanic activity capacities. While the CH content in the control mixture slightly increases with age, these values remain significantly lower in

blended cement pastes indicate CH consumption due to pozzolanic reactions in the system.

Hardened cement pastes with NP showed low CH contents at 3 and 28 days. This is attributed to the fact that NP rapidly consumes the CH formed in the system due to its high reactivity and high amorphous silica content (71.21% SiO₂) and promotes the formation of secondary C-S-H gel. The low CaO content (0.22%) of NP does not provide additional calcium contribution to the system; therefore, CH formation depends solely on clinker hydration, and the observed consumption of CH displays the high pozzolanic reactivity of NP. In addition, the almost complete depletion of CH content in 28 days, especially at high substitution levels such as 40%, of NP is attributed to its high pozzolanic activity. The CH content in BFS blended cement pastes remained at higher levels than NP. BFS, due to its relatively high CaO content, may provide additional calcium ions during hydration, which can support clinker hydration and may indirectly contribute to the CH levels in the system while also participating in pozzolanic reactions. However, this contribution is rather limited, and the main source of CH in the system remains the clinker hydration [138, 139].

CH content in CC blended cements remained higher than that of NP blended cement, similar to BFS, and lower than the control mixture. High SiO₂ (CC1: 58.94%; CC2: 62.47%) and Al₂O₃ (CC1: 31.90%; CC2: 25.54%) content of CC contributes to the consumption of CH by increasing the pozzolanic reaction capacity. Over time, increasing pozzolanic reactions in both BFS and CC blended systems enhance CH consumption, resulting in similar CH levels in both systems by the end of 28 days. According to Tironi et. al, calcined clays consume different amounts of CH depending on several factors, including their mineralogical structure, crystal structure order, specific surface area, and thermal treatment conditions. Although a high surface area and amorphous structure increase CH consumption, not every high CH consumption is directly reflected in increased mechanical strength. Instead, the strength develops mainly due to the filling and densification effects of the reaction products within the microstructure [134].

The findings obtained show that normalized CH content is a reliable parameter in terms of evaluating the pozzolanic reaction capacity in the system. While NP maximizes CH consumption due to its high amorphous silica content and high pozzolanic reactivity, BFS tends to maintain slightly higher CH levels by balancing its pozzolanic activity with

the hydration reactions in the system. Calcined clay increases CH consumption through its high reactivity, resulting in moderate CH levels compared to the control. These findings indicate that different SCM types can significantly influence the balance of hydration products and the overall pozzolanic reaction mechanisms in cementitious systems.

Table 5.2 CH contents of control and blended cement pastes with different SCM types at 3 and 28 days

Cement type	CH content (%)		Normalized CH content (%)		Relative CH content (%)	
	3 days	28 days	3 days	28 days	3 days	28 days
PC2_control	15.0	15.4	15.0	15.4	100.0	100.0
NP20_120min	9.0	7.0	11.3	8.8	75.3	57.1
BFS20	10.8	8.6	13.5	10.8	90.0	70.1
CC120	10.0	9.5	12.5	11.9	83.3	77.3
CC220	9.6	8.4	12.0	10.5	80.0	68.2
NP40_120min	4.1	0.7	6.8	1.2	45.3	7.8
BFS40	8.6	5.8	14.3	9.7	95.3	63.0

5.2.3 Influence of SP content or w/b ratio

One of the most critical parameters determining the properties of cementitious systems in fresh and hardened states is the water/cement (w/c) and water/binder (w/b) ratio. These ratios express the mass ratio between the amount of water in the mixture and the amount of cement or total binder. They are the main determinants of the degree of hydration, microstructure development, mechanical strength, and durability in the system. In particular, the w/b ratio directly affects the hydration conditions by determining the average distance between the binder particles in the system. Lower w/b ratios allow cement particles to settle closer to each other, allowing hydration products to combine in short distances and establish strong bonds and to form a matrix with low porosity. This allows high strength to be achieved even if not all cement particles in the system are fully hydrated. In blended cements, the importance of w/b ratio increases due to the high-water

requirements of SCMs. Using SCMs such as pozzolanic materials or slag instead of cement clinker initially dilutes the amount of Portland cement in the system and may limit the hydration rate and early strength in the short term. However, in the long term, SCMs react with Ca(OH)_2 released during cement hydration to form secondary C-S-H gels. This process contributes to the increase in strength by increasing the amount of hydration products and binding properties [140]. Therefore, the increase in the w/b ratio increases the amount of free water in the system, increasing ion mobility and allowing the hydration reactions to proceed. In systems containing SCM, this progress can increase the production of Ca(OH)_2 in the system, together with pozzolanic reactions, or affect the CH content by supporting consumption.

The CH contents of the control cement paste (PC1_control) and blended cement pastes with different w/b ratios at 3 and 28 days of age, along with the CH values normalized to the Portland cement ratio and the calculated relative CH contents, are presented in Table 5.3. The effect of the increase in w/b ratio on the normalized CH content in the control cement pastes is limited. The increase in the water/cement ratio contributes to more free water in the mixture and the formation of a suitable environment for the hydration reactions to proceed. However, the total amount of Ca(OH)_2 produced in the system by cement remains limited even if the amount of water increases. This situation shows that the increase in w/b ratio does not significantly increase the normalized CH content, although it partially increases hydration. The fact that the normalized CH content does not show dramatic differences in both early and late ages reveals that the increase in w/b ratio in the control pastes has a limited effect on CH production.

In blended cement pastes, the increase in the w/b ratio has a more pronounced effect on the normalized CH content. Due to the use of pozzolanic materials in blended cement systems, a higher amount of water is required for both hydration and pozzolanic reactions to proceed. A higher w/b ratio increases the amount of water in the system, increasing ion mobility, and this increase meets the high-water demand of the system and contributes to the progress of the reactions. Although pozzolanic reactions consume a portion of the formed Ca(OH)_2 , the progress of the hydration degree, thanks to the increasing w/b ratio, increases Ca(OH)_2 production in the system. Therefore, a significant increase is observed in the normalized CH content in blended cement pastes as the w/b ratio increases. In addition, the progress of hydration reactions partially balances the Ca(OH)_2 consumption

effect of pozzolanic reactions and contributes to the increase in the CH amount in the system.

In the comparison of control and blended cement pastes, it is seen that the normalized CH contents of blended cement pastes are lower than those of control pastes at all w/b ratios. The main reason for this is that the cement clinker ratio is lower in blended cement systems, and some of the CH is consumed due to pozzolanic reactions. However, as the w/b ratio increases, the normalized CH content in blended cement pastes closer the control pastes. This situation reveals that the increase in w/b ratio in blended cement systems has a significant effect on hydration and that the potential hydration capacity of the system can be used more effectively at high w/b ratios.

Table 5.3 CH contents of control and blended cement pastes with different w/b ratios at 3 and 28 days

w/b ratio	CH content (%)		Normalized CH content (%)		Relative CH content (%)	
	3 days	28 days	3 days	28 days	3 days	28 days
PC1_control_0.45	14.7	15.2	14.7	15.2	100.0	100.0
PC1_control_0.50	14.5	14.9	14.5	14.9	100.0	100.0
PC1_control_0.55	14.7	15.3	14.7	15.3	100.0	100.0
BC_0.45	9.3	7.0	11.6	8.8	78.9	57.9
BC_0.50	10.4	7.9	13.0	9.9	89.7	66.4
BC_0.55	11.2	8.5	14.0	10.6	95.1	69.3

5.3 Influence of Superplasticized Blended Cementitious Systems on Compressive Strength

In high-performance cementitious systems, compressive strength, particularly at early and late ages, is a critical indicator of both structural safety and long-term durability. Therefore, a detailed evaluation of the interactions between the components on strength development is crucial. The compressive strength of cementitious systems is directly related not only to the amount and type of cement but also to the type and dosage of chemical or mineral admixtures used in the mixture. SCMs used as replacement materials in blended cements generally reduce early-age strength due to reduced cement content and slow kinetics of pozzolanic reactions. However, they are known to increase strength in the long term through pozzolanic reactions. These trends are consistent for most SCMs, including fly ash, metakaolin, and agricultural waste ash. The effect of SCMs on compressive strength varies depending on the type of SCM, replacement level, particle size, and environmental conditions [8]. On the other hand, SCMs can negatively impact rheological properties due to their high-water requirement. In this context, superplasticizer (SP) provides high workability with a low water/binder ratio while also directly affecting compressive strength by increasing the matrix density of cementitious systems. SPs increase the homogeneity of the fresh state of the cementitious system by dispersing the binder particles and limiting the formation of porous structures. These mechanisms allow for more effective hydration, especially at early ages, and support strength development. The performance of superplasticizers in blended cement systems is heavily influenced by their compatibility with factors such as the type of SCMs, cement composition, chemical composition of admixtures, particle size, fineness, etc. This compatibility plays a key role in determining the workability of the fresh state of the cementitious system and the strength and durability of the hardened cementitious material [9, 22].

The superplasticizer types used in this study include poly-naphthalene sulfonate (PNS), poly-melamine sulfonate (PMS), polycarboxylate (PCE), and leonardite humic acid (LHA) admixtures. These admixtures generally have different dispersion mechanisms. PNS and PMS admixtures provide dispersion by creating electrostatic repulsion between cement particles. On the other hand, PCE offers high dispersion

capabilities through electrostatic interaction and steric hindrance, particularly due to their long side chains; steric effects play a dominant role in this group of admixtures. LHA are among the admixtures that can simultaneously exhibit electrostatic and steric effects, with a more complex and variable interaction profile depending on their chemical structure. These differences are the main factors that determine the interaction of the admixture with the binder surface and, therefore, the rheological behavior and mechanical performance of the system. The effectiveness of the SCMs is as follows: The surface properties of the SCM used are directly related to its particle size and chemical composition. Therefore, the interaction between the admixture type and the SCM plays a decisive role in cementitious systems' early- and late-age compressive strength. This section investigates the effects of different superplasticizer types on the strength of blended cement mixtures containing different SCMs.

Compressive strength tests were conducted on hardened cement paste specimens at 2, 7, 28, and 90 days. Two Ø34×60 mm cylindrical samples were tested for each age, and the average strength was reported. In this study, the large number of input parameters combined with testing 144 compressive strength samples are complicated straightforward comparisons among different mix designs. Therefore, a correlation matrix approach based on variable prioritization was adopted. Thus, linear relationships between independent variables in the system and compressive strength at 2, 7, 28, and 90 days, which are the compressive strength outputs, were systematically analyzed. The correlation matrix serves as a methodological filtering tool that allows determining and interpreting which variables significantly affect compressive strength by distinguishing the degrees of influence of inputs in multivariate systems. The correlation matrix, which quantitatively shows the linear relationships between the input variables and the four outputs demonstrating the compressive strength, is presented in Figure 5.10.

According to the correlation matrix, it is seen that the compressive strength of superplasticized blended cementitious systems is correlated with different inputs at different ages. Among the variables with the highest correlation coefficients in early age (2 and 7 days), strengths, w/b ratio, SCM d_{10} (particle fineness), and OPC content (or SCM replacement level) stand out. In particular, the strong negative relationship between w/b ratio and compressive strength shows that low water/binder ratios significantly increase compressive strength by increasing early hydration and matrix density. Similarly, finer particles SCMs (lower d_{10} value) support early age strength not only by

having higher pozzolanic reactivity, but also by means of the filler effect that increases density by filling the matrix voids. On the other hand, OPC content reflects the dominant effect of the cement amount on the hydration process, especially in the first days. In addition, it has been observed that the use of PCE and LHA, which are among the SP admixture types, also significantly affects compressive strength at some ages. While PCE, in particular, shows a positive correlation at early ages and supports strength with its dispersion capacity and water-reducing effect. The interaction of the LHA with the cementitious system is more complex and can have either positive or limiting effects depending on the compatibility between the admixture and the binder type.

At late-age strengths (28 and 90 days), chemical composition becomes prominent; a significant positive correlation is observed between the SCM $\text{SiO}_2 + \text{Al}_2\text{O}_3$ content and compressive strength. This confirms the known effect of pozzolanic reactions that increase strength over time. Furthermore, physical parameters such as w/b ratio and SCM particle size appear to maintain their influence at late ages. In this study, superplasticizer (SP) dosages were not randomly selected; they were determined through mini-slump tests to ensure similar fluidity at different w/b ratios. Therefore, SP content and w/b ratio cannot be considered completely independent variables in the correlation matrix. This suggests that caution should be exercised, especially when interpreting these two parameters together. When all ages are evaluated together, it is determined that SP content is determined depending on the w/b ratio, SCM d_{10} , and SCM $\text{SiO}_2 + \text{Al}_2\text{O}_3$ (due to SCM type) content parameters exhibit significant correlations with all four compressive strength outputs. Therefore, these three inputs stand out as the most decisive common parameters, as they represent both physical and chemical properties and consistently influence compressive strength development across all ages. Based on these inputs (w/b ratio, SCM d_{10} , and SCM type), the samples that best represent the system and reflect the variable distribution were selected from 144 different compressive strength samples; the results are presented only on these selected mixtures.

	OPC content	PNS	PMS	PCE	LHA	SP content	SCM d ₁₀	w/b ratio	SCM SiO ₂ +Al ₂ O ₃	2-day/ 7-day/ 28-day/ 90-day
OPC content	1.00									
PNS	-0.02	1.00								
PMS	-0.06	-0.30	1.00							
PCE	-0.06	-0.30	-0.33	1.00						
LHA	-0.06	-0.30	-0.33	-0.33	1.00					
SP content	0.02	0.07	0.08	-0.31	0.27	1.00				
SCM d ₁₀	-0.59	0.01	0.08	0.08	0.08	-0.44	1.00			
w/b ratio	-0.17	-0.08	0.02	0.02	0.02	-0.44	0.25	1.00		
SCM SiO ₂ +Al ₂ O ₃	0.03	0.11	0.06	0.06	0.06	0.54	-0.22	-0.30	1.00	
2-day	0.55	-0.07	0.03	0.11	-0.11	0.28	-0.41	-0.63	0.15	1.00
7-day	0.48	0.00	-0.01	0.11	-0.15	0.41	-0.49	-0.77	0.31	1.00
28-day	-0.06	0.00	-0.02	0.23	-0.20	0.13	-0.13	-0.63	0.25	1.00
90-day	-0.07	0.09	-0.02	0.18	-0.22	0.20	-0.14	-0.69	0.28	1.00

Figure 5.10 Correlation matrix plot between inputs and 2-day, 7-day, 28-day and 90-day compressive strength outputs

5.3.1 Influence of SP content or w/b ratio

Low water/binder (w/b) ratios reduce the distance between cement and SCM particles, allowing the products formed by hydration to come into contact quickly and producing a dense microstructure. This density is particularly pronounced at very low w/b ratios such as 0.20–0.30; at these ratios, the bonds formed between cement particles dramatically increase the strength of the concrete, and in some cases, fracture can occur in the aggregate. However, this high performance can only be achieved in blended cements containing SCM by providing prolonged and moist curing conditions. This is because SCMs, such as fly ash and blast furnace slag, have low reactivity, and it takes time for them to interact with the calcium hydroxide released from cement hydration to form secondary C-S-H phases. For this reason, early-age strength is relatively low in SCM blended cement, but the strength increase continues over time with appropriate curing. Today, the w/b ratio can be reduced thanks to superplasticizer admixtures; this allows for more efficient development of hydration products with higher binder density in SCM-blended cement, supporting the production of more durable, low-permeability concretes in the long term [140]. Indeed, in this study, the effect of the w/b ratio on compressive strength was investigated on blended cement pastes, emphasizing its decisive role in system performance.

Figure 5.11 and Figure 5.12 present the compressive strength results of blended cement (BC) pastes containing 20% NP_120min and 20% BFS, prepared at different water/binder ratios and tested at 2, 7, 28, and 90 days, respectively. In these blended cement mixtures containing both NP and BFS, PCE was used as a superplasticizer, and the SP type was kept constant to prevent SP-induced effects from being included in the comparison. In addition, control samples with different water/cement ratios were included in both figures and evaluated as a reference without additives. As seen in Figure 5.11, an increase in the w/b ratio significantly decreased the compressive strength of both the NP blended cements and the control samples. At the low w/b ratio (0.40), BC paste reached 50.0 MPa after 90 days of curing, exhibiting a compressive strength approximately 44% higher than the control sample. This increase can be explained by the denser microstructure resulting from the decreased distance between the binder particles and the progression of pozzolanic reactions. Furthermore, the low w/b ratio promotes the densification of the binder phases, reducing the void ratio and accelerating the interactions

between the cement and SCM particles. While a decrease in the overall strength of the system was observed with the increase in the w/b ratio to 0.45, the BC systems showed slightly higher strength compared to the control sample on day 28. This difference indicates a period during which the natural pozzolan reacted with the calcium hydroxide released during the hydration process, contributing to the formation of secondary C-S-H. However, increasing the w/b ratio to 0.50 severely limited strength development in both systems. This decrease can be attributed to the higher water content, which increases the void ratio in the cement paste and disrupts the continuity of the hydration products, weakening the microstructure. Furthermore, increasing the distance between binder particles reduced the efficiency of pozzolanic reactions, limited ionic interactions, and suppressed the positive effect of natural pozzolan. When 2-day compressive strength results were evaluated at all w/b ratios, systems containing natural pozzolan exhibited similar or higher early-age strengths compared to control samples. This result can be attributed to the increased specific surface area of natural pozzolan after 120 minutes of grinding, which, despite its limited participation in early-age chemical reactions, results in a denser cement matrix through its filler effect. In conclusion, the data obtained suggest that low w/b ratios in BC systems not only increase binder density but also enhance the effectiveness of the pozzolanic reactivity, playing a decisive role in long-term strength.

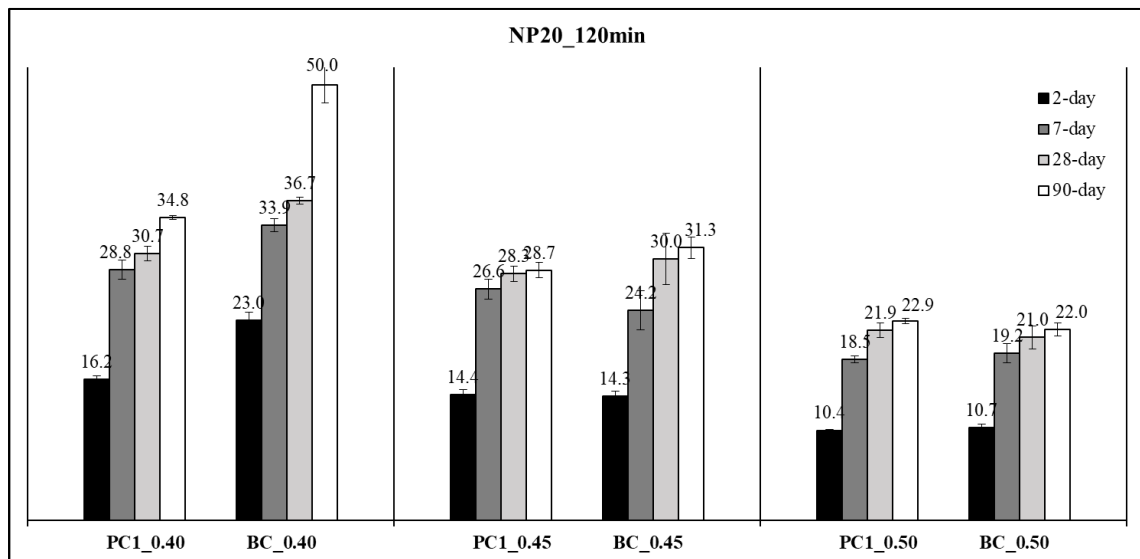


Figure 5.11 Compressive strength of PC1 control and blended cement with NP_120min at different w/b ratios, tested at 2, 7, 28, and 90 days

Figure 5.12 shows the compressive strengths of blended cement systems (BC) containing 20% blast furnace slag (BFS) at different water/binder (w/b) ratios (0.40, 0.45,

and 0.50) after 2, 7, 28, and 90 days of curing. Control mixtures (PC1) containing only Portland cement for each w/b ratio are also presented in the figure for comparison. The data obtained show that strength development is extremely sensitive to the w/b ratio. The blended system (BC_0.40), prepared at the lowest w/b ratio of 0.40, reached a compressive strength of 49.2 MPa at the end of 90 days of curing, exhibiting approximately 41% higher strength than the control sample (34.8 MPa). This positive contribution of BFS was achieved despite the partial reduction of the cement content in the binder system and was supported by the activation of pozzolanic and latent hydraulic reactions in the long term. A decrease in strength was observed at all ages when the w/b ratio was increased to 0.45. However, the 90-day strength of the BC system (31.4 MPa) remained above that of the control mixture (28.7 MPa). The increase in compressive strength in the blended cement system was particularly pronounced at day 28. This difference can be explained by the delayed reaction of BFS with hydration products, which has contributed to the formation of C-S-H over time. However, this effect is limited to the early ages. Increasing the w/b ratio to 0.50 significantly limited the compressive strength development in both control and BC. Comparing the 90-day strengths, the BC reached 27.6 MPa, while the control mixture remained at 22.9 MPa. In this context, while the relative superiority of the BFS was maintained, the strength of all ages decreased significantly. This can be explained by the fact that a high w/b ratio increases the void ratio in the cement paste, reducing both hydration efficiency and negatively affecting the reaction conditions of the slag. The increased water content increases the distance between the binder particles, limiting contact between the slag and the hydration products and slowing down the overall reaction kinetics of the system.

Furthermore, when the 2-day results were evaluated, it was noteworthy that the systems with BFS exhibited higher early-age strength compared to the control samples at all w/b ratios. This has been explained in the literature by the BFS exhibiting a certain hydraulic activity at early ages. BFS, which partially reacts in the presence of calcium hydroxide in an alkaline environment, can contribute to the formation of C-S-H at early ages. Furthermore, the fine particle size of the BFS used provides a filler effect in the mixture, resulting in a denser matrix structure. Thus, both physical and chemical effects combined to result in higher early-age strength compared to the control mixture [141].

The findings of this study demonstrate that BFS can positively impact not only long-term but also early-age compressive strength of cementitious systems under certain

conditions. The higher compressive strength observed in BFS blended cements compared to the control sample, particularly at 2 and 7 days, demonstrates that the BFS can react, albeit limitedly, at early ages and can densify the microstructure through its physical filler effect. However, the significant and permanent effect of the BFS on compressive strength is more pronounced at late ages. Furthermore, the BFS effect was observed to be stronger at lower w/b ratios, indicating that lower void volume and denser particle support BFS reactivity. Therefore, when the BFS and w/b ratio are evaluated together, a synergistic relationship emerges, triggering both physical and chemical interactions in the system's strength development.

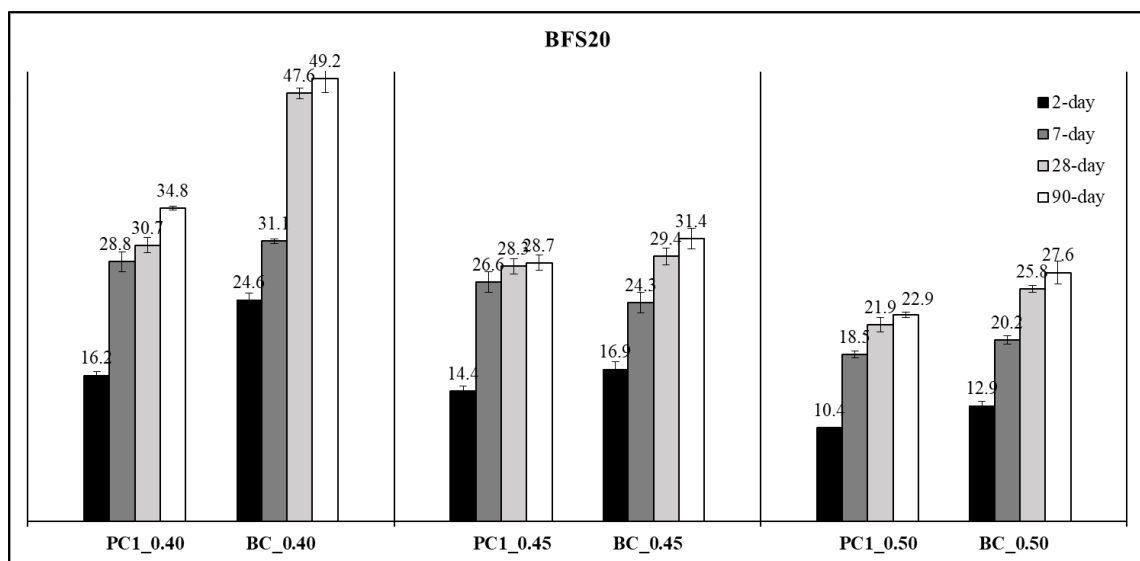


Figure 5.12 Compressive strength of PC1 control and blended cement with BFS at different w/b ratios, tested at 2, 7, 28, and 90 days

5.3.2 Influence of SCM particle size (SCM d_{10})

The performance of SCMs varies significantly not only depending on their chemical composition but also on their physical properties, particularly their particle size. According to Liu et al., particle size determines SCM reactivity, participation in the hydration process, and its impact on microstructure and mechanical properties. Fine particle size SCMs have been found to participate more effectively in pozzolanic/hydraulic reactions by increasing the reaction surface area due to their higher specific surface area, and to improve the pore structure of the matrix through their physical filling effect. In this context, the fineness of SCMs stands out as a critical

variable that directly affects key performance parameters such as early and late-age strength development, hydration kinetics, and durability [142].

Figure 5.13 presents the compressive strength results of blended cement (BC) pastes incorporating 20% natural pozzolan ground for 60 and 120 minutes (NP_60min and NP_120min), tested at 2, 7, 28, and 90 days. In these blended cement mixtures, PCE was used as the superplasticizer, and the SP type was kept constant to eliminate any potential influence of the admixture on the results. All mixtures were prepared with a constant w/b of 0.45. NP_60min BC exhibited lower strength compared to the control sample at all ages; however, the 120-minute ground NP containing BC produced higher values than the control sample, particularly at 28 and 90 days. Furthermore, the NP_120min BC achieved comparable results to the NP_60min BC at earlier ages. This difference is directly related to the change in fineness of the SCM with grinding time. Indeed, when the fineness values are examined, the d_{50} value decreases from 7.1 μm to 5.2 μm and the d_{90} value decreases from 60.3 μm to 45.7 μm as the grinding time is increased from 60 to 120 minutes. This fineness increases the reactive surface area of the SCM and supports its physical filler effect within the cement paste, reducing porosity. In particular, increasing the finer fractions ($d_{10} = 0.7 \mu\text{m}$) increases the SCM's pozzolanic reactivity and supports its filling effect. As a result, the contribution of natural pozzolan to compressive strength development becomes important when evaluated not only with chemical reactivity but also with microstructural compaction that develops depending on particle size distribution. These findings demonstrate that the effect of natural pozzolan in cement systems can only be effectively realized when sufficient fineness levels are achieved, and that the physical-chemical activation potential of the SCM is mainly dependent on grinding parameters. Although early-age strength is generally expected to be low in blended cementitious systems, the results obtained in this study demonstrate that SCMs to the appropriate fineness level can significantly overcome this limitation through physical mechanisms. This is an extremely valuable and noteworthy finding for studies to improve the early-age performance of blended cementitious systems.

A study by Liu et al. showed that increasing the fineness level significantly increases reactivity for both BFS and NP. Finely ground BFS exhibits higher reactivity at early ages, reacting more effectively with hydration products and increasing the density of the microstructure through physical packing. Similarly, natural pozzolans, especially when they reach sufficient fineness levels, have been shown to participate more

effectively in pozzolanic reactions and promote secondary C-S-H formation. For both types of SCMs, increasing fineness both expands the chemical interaction surface and decreases the void ratio in the microstructure. These findings demonstrate that particle size in SCMs determines not only physical but also reactivity performance parameters [142].

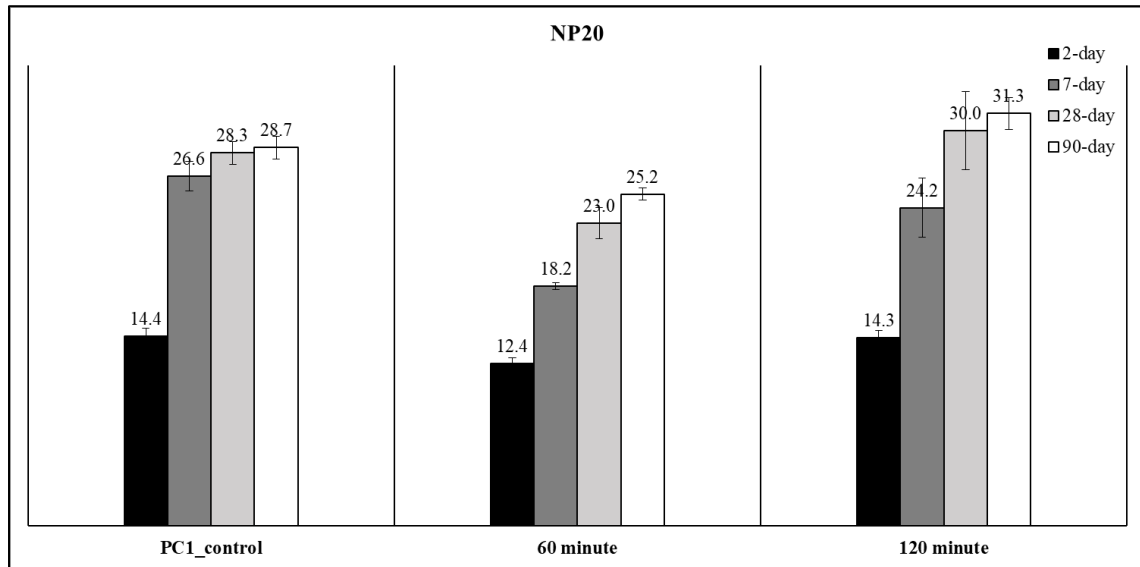


Figure 5.13 Compressive strength of PC1 control and blended cement with 20% NP with different particle sizes (achieved by 60 and 120 minutes of grinding), tested at 2, 7, 28, and 90 days

5.3.3 Influence of SCM type

In cementitious systems, the type of SCM plays a significant role in both the hydration kinetics and compressive strength. The chemical composition, mineralogical structure, and fineness of the SCM used directly influence the extent to which the SCM interacts with the cementitious system. In this context, even when used at the same replacement level, SCMs from different sources can differ in the type and amount of additives they contribute to the cement matrix. Therefore, the appropriate selection of the SCM type is critical for both early- and late-age compressive strength. Figure 5.14 illustrates the compressive strength development of cement pastes incorporating different SCM types (NP_120min, BFS, and CC1) and control cement paste (PC1), tested at 2, 7, 28, and 90 days. In all blended cements shown in Figure 5.14, the SCM replacement level was 20%, and the water/binder ratio was 0.45 in both the blended cement and PC control mixtures. In addition, PCE was used as a superplasticizer in all blended cement mixtures.

The NP_120min blended cement exhibited similar early-age performance to the control mixture, with values of 14.3 MPa and 24.2 MPa at 2 and 7 days, respectively. However, the NP_120min blended cement mixture appears to have slightly surpassed the control mix at 28 and 90 days. This performance improvement can be attributed to the increased specific surface area and reactivity resulting from reduced d_{50} to 5.2 μm after 120 minutes of grinding the natural pozzolan with a high SiO_2 content (71.21%). Fineness enhanced pozzolanic reactions, and the matrix density increased, particularly at later ages, through secondary C-S-H formation. Also, it contributed to compressive strength through the early-age filling mechanism. BFS blended cement exhibited slightly higher early-age strength compared to the natural pozzolan. This difference can be attributed to the latent hydraulic activity of BFS. The 28- and 90-day values are quite similar to those of NP. Furthermore, considering the particle size, BFS has a d_{50} value of 10.8 μm , making it coarser than NP, but its d_{90} value of 25.7 μm is significantly lower than NP. This may have optimized the filling effect by providing a more homogeneous structure where larger particles are confined. Thus, BFS exhibited a more even strength development between early and late ages. Among the SCM types, calcined clay (CC1) provided the highest compressive strength. For CC1 blended cement pastes, values reached 46.6 MPa on day 7 and 48.1 MPa on day 90, representing approximately 75% and 67% higher compressive strengths, respectively, than the control mixture. Calcined clay exhibits a high pozzolanic character with a higher content of silica and alumina. Furthermore, its particle size distribution reveals that it is finer than other SCMs ($d_{50} = 4.0 \mu\text{m}$). This fineness accelerated the reactive behavior of the CC1, especially from day 7 onward, and enabled remarkably high strength levels to be achieved at 28 and 90 days.

Comparing all blended cements, it is clear that both chemical composition and particle size distribution are key factors in the performance of the SCMs. Enhanced fineness of natural pozzolans significantly improves their effectiveness in contributing to compressive strength development. BFS demonstrated balanced compressive strength contribution at both early and late ages. CC1 achieved high strength at both early and late ages and demonstrated superior performance among SCM types. The reason for this superiority can be attributed to the high level of fineness of CC1, together with its high amount of silica and alumina. These findings suggest that parameters such as fineness, chemical composition, and mineralogical structure should be evaluated together for the effective use of SCMs.

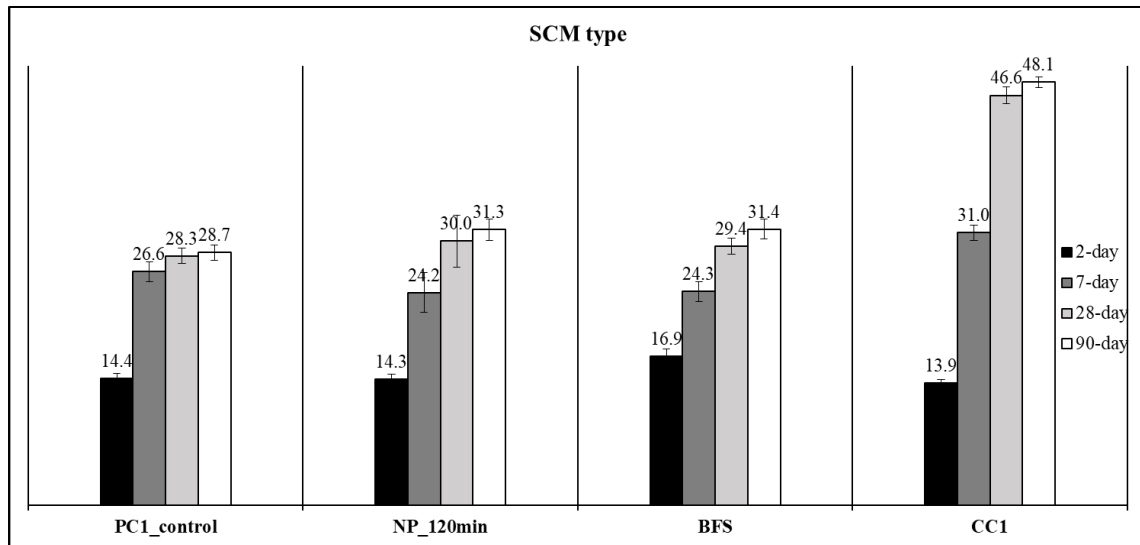


Figure 5.14 Compressive strength of PC1 control and blended cement with various SCMs at 20% replacement level, tested at 2, 7, 28, and 90 days

5.4 Machine Learning-Based Performance Evaluation

Machine learning (ML), a subset of artificial intelligence (AI), is widely applied in civil engineering to predict various outputs of cementitious systems. Machine learning methods are trained on large databases of laboratory and field data using input factors, increasing prediction accuracy. Furthermore, it has been stated that the accuracy of the models used is related to the quality of the datasets on which they are trained. That model's performance can be further improved with larger datasets. Machine learning applications support experimental processes in civil engineering, improving prediction accuracy while saving time and resources. Their ability to identify patterns and relationships in large data sets makes them effectively used in predicting the properties of complex materials like concrete and optimizing mix designs. This allows for early identification of potential problems and the development of more efficient and cost-effective solutions, making machine learning methods valuable as innovative tools in civil engineering applications [143, 144].

Regression analysis, within machine learning models, is used as a useful tool for predicting various mechanical properties and performance parameters of cementitious systems. Regression enables accurate predictions across diverse datasets by mathematically modeling the relationships between input and output variables.

Regression models such as support vector machine (SVM), Gaussian process regression (GPR), and artificial neural network (ANN) are effectively used to process high-dimensional data, reduce error rates, and identify complex relationships. These methods analyze the effects of inputs such as cement, water, mineral admixtures, and aggregate ratios on outputs such as compressive strength, tensile strength, flexural strength, modulus of elasticity, and hydration kinetics, enabling rapid and reliable prediction of cementitious system performance [96, 145, 146]. The use of admixtures (SCM or superplasticizer) in cementitious systems predicts blended cement's performance more complex; therefore, more advanced computational techniques are required to develop prediction equations. At this point, ML, as a new and emerging tool, will be used for regression analysis to determine the interrelationships between the characteristic parameters that govern the compatibility of the components with the help of MATLAB software. The complexity of cause-and-effect relationships due to the high number of parameters and interactions makes it very advantageous to use machine learning tools as an innovative approach to this complexity. It is thought that this will facilitate a better understanding of the compatibility parameters, which are the focus of the thesis, and the design of component types and compositions of low-carbon high-performance cements.

This section presents the results of regression analyses performed on datasets obtained from isothermal calorimetry, thermal analysis, and compressive strength tests. A total of 29 regression models from six different algorithm families were evaluated using 10-fold cross-validation, with hyperparameter optimization applied where applicable. Following these analyses, the two models with the highest predictive accuracy were identified for each dataset, and only these models were reported to maintain the focus of the study. The hyperparameters of the models whose results are presented in Section 5.4.1 are given in Table 5.4. Hyperparameters provide a transparent display of the settings that directly impact model performance, enabling objective comparisons between models. Furthermore, this information facilitates reproducibility, allowing researchers to replicate and optimize model setups on similar datasets accurately. Additionally, the evaluation of the importance of features on model predictions is presented to enhance the developed models' interpretability and provide insights into the key parameters affecting the performance of cementitious systems.

Table 5.4. Hyperparameters of models

Model	Hyperparameter	Values
Fine Tree	Minimum leaf size	4
Boosted Tree	Ensemble method	Boosted
	Minimum leaf size	8
	Number of learners	30
Wide NN	Hidden layer	1
	Node number	100
	Activation function	ReLU
Bilayered NN	Hidden layer	2
	Node number	10,10
	Activation function	ReLU
Medium NN	Hidden layer	1
	Node number	25
	Activation function	ReLU
Trilayered NN	Hidden layer	3
	Node number	10, 10, 10
	Activation function	ReLU
Exponential GPR	Basic function	Constant
	Kernel function	Exponential
Medium Gaussian SVM	Kernel function	Gaussian
	Kernel Scale	3
Cubic SVM	Kernel Scale	3

5.4.1 Evaluation of Regression Model Performance

5.4.1.1 Isothermal Calorimetry Dataset Results

Cement hydration is a fundamental process that occurs through the exothermic reaction between cement and water, leading to the development of compressive strength. Temperature changes experienced in the early stages of the hydration process can directly affect the strength loss, shrinkage, and cracking behavior of concrete. Therefore, accurate prediction of cement hydration kinetics is critical to preventing field setting delays, strength variability, cracking, and long-term durability problems. The unpredictability of the hydration process can lead to workability issues and temperature-related problems. Concrete cracks, caused by drying shrinkage and settlement due to inaccurate prediction

of hydration temperature, are known to initiate between 3 and 56 days after concrete placement. Therefore, developing a comprehensive modeling framework to understand hydration kinetics is crucial for preventing such problems and improving process management [147].

During the regression analysis of isothermal calorimetry results, a dataset consisting of 310 data points with 7 input variables and 4 output variables was evaluated. The input variables are: OPC content (%mass); SP type; SP content (%); SCM d_{50} (μm); water/binder ratio; SCM $\text{SiO}_2+\text{Al}_2\text{O}_3$ content (%); and SCM CaO (%) content. The outputs are onset time (min), onset heat (mW/g cement), induction period (min), and total heat at 72 h (J/g cement). The results of three statistical parameters – RMSE, mW/g cement or J/g cement, R^2 , unitless, and MAE, mW/g cement or J/g cement - used to evaluate all models are presented in Table 5.5 for onset time, onset heat, induction period and total heat at 72 h. Lower values for RMSE and MAE and higher values for R^2 generally indicate better model performance. For all regression classes in MATLAB software (given in section 4.4), the results of the model that gives the two best results of different classes are given. Models for all outputs (onset time, onset heat, induction period, total heat at 72 h) were analyzed as 20/80 split test/training set. Table 5.5 presents a comparison of the prediction results for both training and test results of the two best-performing models for each output of the isothermal calorimeter test.

The training results obtained with 10-fold cross-validation, reported in Table 5.5, are critical for assessing the error levels of the models during the training process and their ability to learn data patterns. These results allow for the identification of overfitting or underfitting trends in interpreting test performance. In the onset time predictions, the trilayered NN model achieved RMSE values of 102.18 and R^2 of 0.70 during the training phase. The observed values of RMSE of 50.0 and R^2 of 0.90 on the test set indicate that the model reduces the error on the test data while increasing its explanatory power and provides high generalizability without exhibiting an overfitting tendency. The Exponential GPR model achieved RMSE values of 94.0 and R^2 of 0.74 during training, and RMSE values of 53.33 and R^2 of 0.88 during testing. This suggests that the GPR model similarly demonstrates high accuracy and good generalization on the test data. For onset heat predictions, the trilayered NN model achieved RMSE values of 0.22 and R^2 of 0.63 in training, while achieving RMSE values of 0.07 and R^2 of 0.97 in testing. Despite the relatively low R^2 and high RMSE values during training, the significant improvement

in testing demonstrates that the model has successful prediction capabilities for low-variance, uniformly distributed outputs without overfitting. A similar trend was observed for the Exponential GPR model, with RMSE values of 0.19 and R^2 of 0.73 in training, and RMSE values of 0.07 and R^2 of 0.96 in testing. These results demonstrate that both models perform high accuracy in onset heat predictions and achieve reliable learning. In the induction period prediction, the trilayered NN model achieved 106.37 RMSE and 0.66 R^2 in training, and 44.21 RMSE and 0.95 R^2 in testing, significantly reducing the error while increasing its explanatory capacity. This demonstrates that the model can effectively learn the induction period, which has high variance and complex patterns. On the other hand, the exponential GPR model, exhibited higher test error and lower R^2 compared to the NN model, with 92.12 RMSE and 0.74 R^2 in training, and 63.11 RMSE and 0.89 R^2 in testing. This demonstrates the NN model's superior prediction ability for complex outcomes such as the induction period. The exponential GPR model achieved 18.82 RMSE and 0.69 R^2 values during training and reached 10.12 RMSE and 0.93 R^2 values on the test set for the total heat of hydration at 72 h. The Cubic SVM model performed well with 17.80 RMSE and 0.73 R^2 during training, and 11.14 RMSE and 0.92 R^2 during testing. The significant decrease in RMSE values and increase in R^2 values in the test set compared to the training set for both models demonstrates that the models can make predictions with high generalizability without tending overfitting during the training. Furthermore, the high R^2 values achieved during the testing demonstrate that the models can successfully model outputs with relatively low variance and stable distribution, such as the total heat of hydration. These results show that both exponential GPR and cubic SVM models can be used as a reliable model in total heat of hydration predictions.

Overall, the results demonstrate that the trilayered artificial neural network (NN) model achieves lower RMSE and higher R^2 values on the test data, demonstrating higher generalization success compared to other models. This superior performance of the NN model stems from its high capacity to learn complex and nonlinear relationships. Cement hydration processes exhibit a highly nonlinear structure shaped by the interactions of many parameters, such as temperature, time, water/binder ratio, SCM type, SCM content, SP content, etc. Thanks to its multilayered structure, the NN model can effectively learn the complex relationships between these parameters and precisely obtain the variability that occurs at various stages of the hydration process. Furthermore, the NN model excels

at high-variance outputs, such as onset time and induction period, due to its robust learning capacity to control outliers and capture patterns in the dataset. This shows that neural networks (NN) can provide high accuracy in predicting complex processes such as cement hydration and can be used as a powerful method in data-driven applications where such processes need to be modeled.

Table 5.5. Performance of selected models in predicting hydration kinetics outputs

Output	Model		RMSE	R ²	MAE
Onset time	Trilayered NN	Training*	102.18	0.70	43.29
		Test	50.05	0.90	21.93
	Exponential GPR	Training*	94.0	0.74	39.68
		Test	53.33	0.88	22.60
Onset heat	Trilayered NN	Training*	0.22	0.63	0.13
		Test	0.07	0.97	0.04
	Exponential GPR	Training*	0.19	0.73	0.12
		Test	0.07	0.96	0.05
Induction period	Trilayered NN	Training*	106.37	0.66	51.25
		Test	44.21	0.95	24.05
	Exponential GPR	Training*	92.12	0.74	49.18
		Test	63.11	0.89	33.53
Total heat at 72 h	Exponential GPR	Training*	18.82	0.69	13.17
		Test	10.12	0.93	7.57
	Cubic SVM	Training*	17.80	0.73	12.61
		Test	11.14	0.92	7.71

**With 10-fold cross-validation*

In this study, the models with the best prediction performance, listed in Table 5.5, achieved high accuracy with low error values on both the training and test data sets. The R^2 values above 0.90 for the GPR and NN models on the test sets, in particular, demonstrate that these models are not limited to the data they were trained on but also generalize successfully to the test data. Studies in literature, particularly those using Random Forest (RF) models, have demonstrated high performance in predicting short-term hydration data. RF models achieved strong correlation values ($R^2 > 0.90$) in heat flow and cumulative heat estimations over the first 24 hours; however, their applicability to long-term hydration data was limited. In the study conducted by Cook et al., Random Forest (RF) models, in particular, stood out in short-term hydration predictions, achieving very high accuracy values in 24-hour cumulative heat predictions ($R^2 = 0.979$, RMSE = 14.4 J/g PC). However, the applicability of the RF approach to long-term hydration processes was limited [90, 91]. In contrast, the models developed in this study also demonstrated high performance in 72-hour total heat predictions. The Exponential GPR model demonstrated strong generalization ability with $R^2 = 0.93$ and RMSE = 7.57 J/g PC on the test data, while the Cubic SVM model similarly stood out with $R^2 = 0.92$ and RMSE = 7.71 J/g PC. Therefore, the proposed models were able to predict not only short-term hydration behavior but also longer-term hydration behavior up to 72 hours with reliable accuracy. This demonstrates that these models are more capable of learning nonlinear and multivariate relationships and are more suitable for predicting time-dependent processes. Furthermore, the high level of consistency between the models' performance on the test data and the training data demonstrates that there is no overfitting tendency during the learning process and that the models have strong generalization ability. This is a significant indicator of success for machine learning algorithms, especially those operating on high-variance, multidimensional datasets. Indeed, the ensemble regression model developed by Sun and Lee on fly ash blended cement was trained with 2652 time-dependent data points and achieved successful predictions with low error values, such as RMSE $\approx$ 0.1 and MAE $\approx$ 0.06 mW/g in both the training and testing phases [148]. Similarly, the NN and GPR models used in this study achieved high accuracy levels for outputs such as "onset heat" and "induction period," which are critical for hydration kinetics but have received limited attention in literature.

The fact that NN and GPR models achieved higher prediction accuracy compared to tree-based methods such as RF, which are frequently preferred in literature, is directly

related to the suitability of the algorithms used to the data structure and the problem. The outputs subject to modeling—such as onset time, onset heat, induction period, and 72-hour total heat—represent continuous, time-dependent, and mostly non-linear processes. Regression models such as NN and GPR have an advantage over discrete partitioning-based methods such as RF in estimating such processes in datasets with many variables and complex patterns. Indeed, among the input variables used in this study are SCM type and replacement level, water/binder ratio, SP type, and content, SCM particle size, and SCM chemical composition. Many components directly affecting hydration kinetics are included; these variables' complex, nonlinear interactions increase modeling challenges. The structural flexibility of algorithms like NN and GPR provides a significant advantage in modeling such a multidimensional and physically interactive system. Thanks to their multilayered structures, NN models can successfully learn nonlinear relationships between input variables. GPR, with its kernel-based approach, can flexibly model patterns in the data, improving prediction accuracy. Furthermore, GPR can provide additional information about the confidence level of the prediction by providing uncertainty with each prediction. In contrast, tree-based algorithms like RF generalize by dividing decision boundaries into a limited number of discrete regions; this can limit prediction capacity, particularly in data with subtle transitions and curvilinear changes. Furthermore, while RF models tend to perform well on large and evenly distributed datasets, GPR and NN algorithms demonstrate robust performance even on smaller datasets with high informational density [92, 149]. As a result, it was seen that the predictive performance in modeling depends not only on the mathematical structure of the algorithms but also on the selection of appropriate modeling approaches to the physical variables involved in the hydration process.

Figure 5.15, Figure 5.16, Figure 5.17, and Figure 5.18 present graphs comparing the actual values and predicted values of the models for the best test results in Table 5.5 for onset heat, onset time, induction period, and total heat at 72 h outputs, respectively. These scatter plots, which were used to visually assess model performance, demonstrate a strong correlation between predicted and actual values. Each blue dot in the figures represents a test sample. The fact that the dots lie close to the unit diagonal ($y = x$) line indicates a significant overlap between the predicted and actual values. The data, particularly for the onset heat and total heat at 72 h outputs, are quite close to the line, consistent with both the low error values and strong correlation coefficients shown in

Table 5.5. In the onset time and induction period plots, although some deviations are observed in the high-value extreme examples, the overall distribution largely overlaps the line. This demonstrates that the models maintain their predictive ability not only over narrow time intervals but also over wide and variable time intervals. The fact that the model accurately reflects the general trend, especially for outputs with high variance and a limited sample size, such as the induction period, demonstrates a strong learning capacity. When all graphs are evaluated together, it is seen that the developed models not only adapt to the training data but also successfully generalize to the test data.

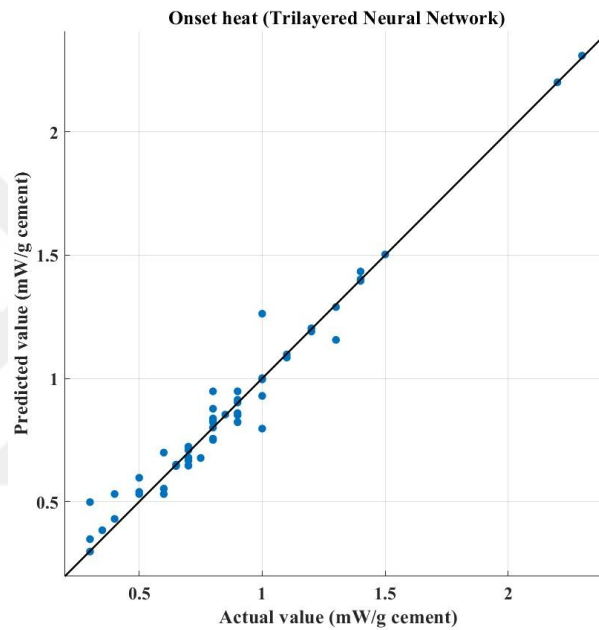


Figure 5.15 Actual vs. predicted onset heat values for the Trilayered Neural Network model

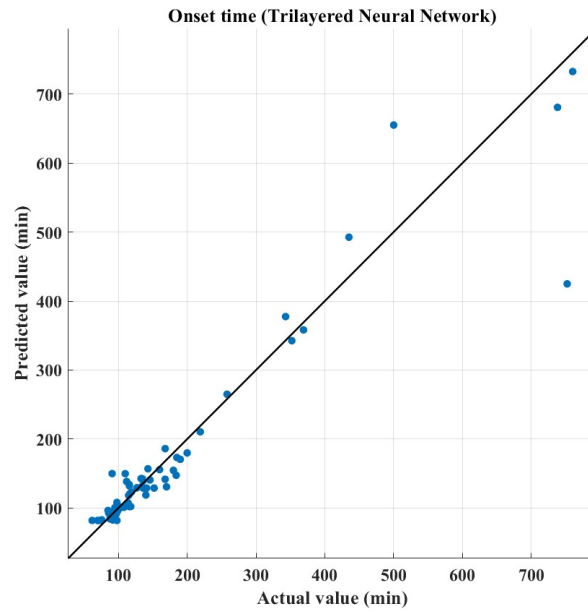


Figure 5.16 Actual vs. predicted onset time values for the Trilayered Neural Network model

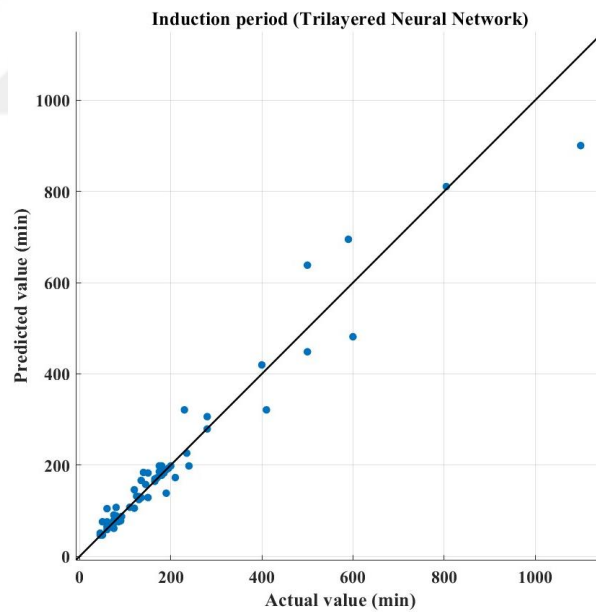


Figure 5.17 Actual vs. predicted induction period values for the Trilayered Neural Network model

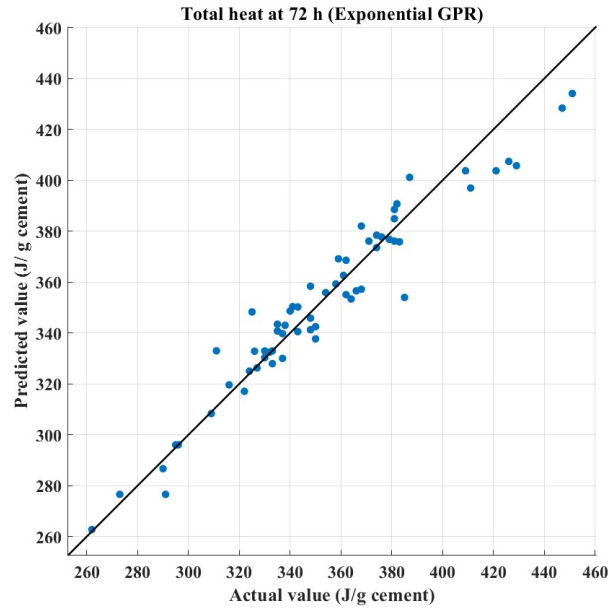


Figure 5.18 Actual vs. predicted total heat at 72 h values for the Exponential Gaussian Regression model

5.4.1.2 Thermal Analysis (TGA) Dataset Results

SCMs reduce the heat of hydration in cementitious systems, can affect workability, and affect durability. However, SCMs not only reduce the amount of cement but also deplete calcium hydroxide (CH) in the mixture through a pozzolanic reaction. However, CH plays a critical role in concrete's resistance to aggressive environmental conditions. Therefore, a balance must be struck between the use of SCM and the amount of CH; both the benefits of the admixture and the protective effect of CH must be utilized [150]. Pozzolanic activity is defined as the reaction of a pozzolan with calcium hydroxide and water to produce additional C-(A)-S-H phases. The level of this activity is determined by the maximum combination capacity with CH and the rate at which this combination occurs. Therefore, interaction with CH plays a fundamental role in both the quantitative measurement and evaluation of pozzolanic activity. Reactivity in this process is influenced by the specific surface area, particle size, and chemical and mineralogical composition of the pozzolan. Therefore, CH is a critical indicator for determining the performance of pozzolanic materials [151].

In this study, CH content was estimated using a regression-based machine learning method. A review of existing literature revealed no comprehensive study directly estimating CH content in this manner. However, considering the reasons mentioned

above, accurate and rapid CH content prediction is of significant importance for cementitious systems (especially in evaluating pozzolanic admixtures and optimizing the durability and long-term performance of cementitious systems). In this context, the proposed method allows CH content prediction without the need for experimental data, presenting a novel approach to the design and evaluation of cementitious systems. The lack of comparable studies in the existing literature highlights the novelty of the proposed method and underlines its potential to make a significant contribution to the field.

During the TGA results analysis, a total of 7 inputs and 2 different outputs were evaluated. The input variables are: OPC content (%mass); SP type; SP content (%); SCM d_{50} (μm); water/binder ratio; SCM $\text{SiO}_2+\text{Al}_2\text{O}_3$ content (%); and SCM CaO (%) content. The outputs are relative CH content normalized as PC amount at 3-day (%) and 28-day (%). The results of three statistical parameters – RMSE, %, R^2 , unitless, and MAE, % - used to evaluate all models are presented in Table 5.6 for relative CH content at 3 and 28 days. Lower values for RMSE and MAE and higher values for R^2 generally indicate better model performance. For all regression classes in MATLAB software (given in section 4.4), the results of the model that gives the two best results of different classes are given. Models for all outputs (relative CH content at 3 and 28 days) were analyzed as 20/80 split test/training set. Table 5.6 presents a comparison of the prediction results for both training and test results of the two best-performing models for each output of the thermal analysis.

Among the models used for 3-day relative CH content predictions, the Exponential Gaussian Process Regression (GPR) model showed the most successful results, achieving the lowest RMSE (3.84) and MAE (2.87) values on the test data. Likewise, the R^2 value achieved by this model on the test data was quite high at 0.94, supporting the overall accuracy of the model. On the other hand, the Medium NN model achieved RMSE values of 4.39 and MAE of 3.44 on the test data, but its R^2 (0.92) was slightly lower than that of the Exponential GPR model. This suggests that Gaussian regression models provide more stable results than neural network models in predicting short-term (3-day) CH amount. A similar trend was observed for the 28-day relative CH content predictions. The Exponential GPR model demonstrated compelling performance on the test data, yielding an RMSE of 4.90, MAE of 3.95, and R^2 value of 0.96. These values demonstrate that the model also offers high accuracy in long-term CH predictions. The bilayered neural network model, while having the same RMSE (4.90) as the GPR model, resulted in a slightly lower MAE (3.80). Also, the test R^2 of 0.96 for both models indicates that their

long-term prediction accuracies are quite similar. However, the higher error values (RMSE = 9.97, MAE = 7.44) were observed in the bilayered NN model on the training data, indicating that despite its high performance on the test set, this model had higher error values during the training process.

In conclusion, the Exponential GPR model appears to provide more balanced and consistent results in both short- and long-term CH content predictions. Neural network models can also provide comparable results, but these models require more data and fine-tuning. In this study, the modeling process for estimating relative CH content was conducted using a multivariate database with structurally complex and nonlinear relationships. Input variables include both continuous and categorical parameters such as binder type (OPC content), superplasticizer type and amount (SCM), particle size (d_{50}), chemical composition ($\text{SiO}_2 + \text{Al}_2\text{O}_3$ and CaO contents), and water/binder ratio. Each of these variables affects the CH content measured in TGA analysis through different mechanisms. In particular, the overlapping effects of various components on mass losses during thermal analysis lead to the emergence of hidden and interactive relationships between CH content and these parameters, which are difficult to express linearly. Indeed, classical methods such as linear regression and multiple linear regression were also tested in the study, but these models performed poorly with R^2 and high error (RMSE, MAE) values. These results demonstrate that the system is inadequate for linear model.

The more stable and successful results provided by Gaussian Process Regression (GPR) models, especially with limited and highly uncertain data, is a frequently emphasized advantage in literature [92]. The GPR model stands out with its low error values and high R^2 values in both 3-day and 28-day relative CH content predictions. This can be attributed to the uncertainty of modeling capability based on the Bayesian approach underlying GPR. Because the GPR model considers not only the mean value but also the confidence interval of the estimate during estimation, it reduces the risk of overfitting, particularly in systems with complex and nonlinear relationships, producing more generalizable results. In addition, the GPR model's efficient evaluation of correlations between data using kernel functions significantly improves model performance, particularly in multifactorial and time-dependent systems such as thermal analysis processes. For these reasons, the GPR model demonstrated higher accuracy and lower error values on the test data in this study compared to neural network models.

Table 5.6 Performance of selected models in predicting relative CH content at 3 days and 28 days

Output	Model		RMSE	R ²	MAE
Relative CH content @3 day	Exponential GPR	Training*	5.94	0.89	4.64
		Test	3.84	0.94	2.87
	Medium NN	Training*	7.37	0.83	5.56
		Test	4.39	0.92	3.44
Relative CH content @28 day	Exponential GPR	Training*	8.26	0.89	6.00
		Test	4.90	0.96	3.95
	Bilayered NN	Training*	9.97	0.85	7.44
		Test	4.90	0.96	3.80

**With 10-fold cross-validation*

Figure 5.19 and Figure 5.20 demonstrate the performance of the Exponential GPR model for 3- and 28-day relative CH content predictions, compared to actual values. In both scatter plots, the majority of the data points are concentrated around the diagonal ($y = x$) line, demonstrating high model accuracy. In particular, for the 3-day predictions (Figure 5.18), the model delivered successful predictions across a wide range of values. However, slight deviations were observed in a few samples with low CH content, which may be attributed to the effects of uncertainties in regions with sparse data. The graph for the 28-day results (Figure 5.19) shows an even stronger trend, with data points converging more closely to the diagonal ($y = x$) line. It is particularly noteworthy that model predictions are highly accurate in the CH content range above 50%. While deviations are found in a few samples at low CH content levels, the overall trend demonstrates that the model can produce reliable output even at these levels. The general trend observed in both graphs supports the GPR model's high generalizability to nonlinear and multivariate systems, and its ability to successfully model complex parameters such as CH content based on TGA data. This level of predictive accuracy demonstrates that the GPR model can effectively learn the interactive and hidden patterns present in the dataset.

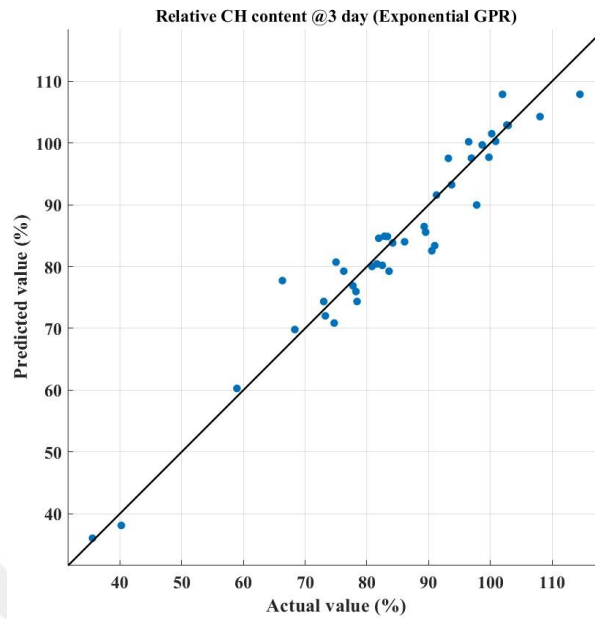


Figure 5.19 Actual vs. predicted relative CH content values at 3 days for the Exponential Gaussian Regression model

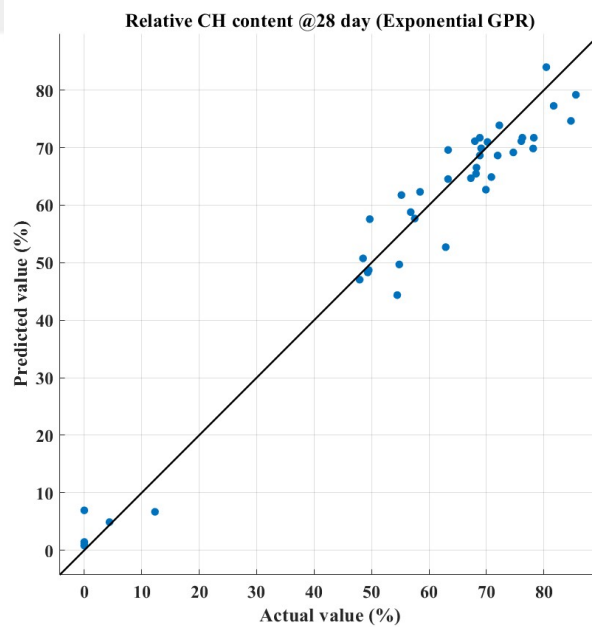


Figure 5.20 Actual vs. predicted relative CH content values at 28 days for the Exponential Gaussian Regression model

5.4.1.3 Compressive Strength Dataset Results

Concrete and cementitious building materials are among the most preferred materials in the construction industry thanks to their high strength, durability, and cost-effectiveness. However, Portland cement production's high energy requirements and CO₂ emissions lead to significant environmental problems. Therefore, substituting a portion of cement with SCM has become an important strategy for developing sustainable building materials. SCMs not only reduce environmental impacts but also play a decisive role in the mechanical and durability properties of cementitious systems, increasing system complexity due to the various interactions between the components. Furthermore, the inclusion of chemical admixtures such as SP further increases system complexity. Furthermore, rapidly and reliably predicting fundamental mechanical properties of cementitious systems, such as compressive strength, poses a significant challenge due to the increased number of components and the complexity of the system.

Compressive strength is the most fundamental criterion for assessing the mechanical behavior of concrete. Concrete is a multi-component and heterogeneous structure containing varying proportions of aggregates, binders, and additives, resulting in non-linear and multivariable relationships between the parameters affecting compressive strength. Therefore, directly obtaining compressive strength using experimental methods is challenging in terms of both time and cost. It also brings with it practical limitations, such as the lack of non-destructive measurement methods for existing structures. To overcome these limitations, attempts have been made to estimate the compressive strength of cementitious systems based on their mix ratios using traditional regression methods. However, the highly non-linear relationship between mix ratios and compressive strength has made it difficult for classical regression models to produce sufficiently accurate results. Furthermore, with the recent development of artificial intelligence, and particularly machine learning algorithms, more flexible and powerful approaches to such complex, pattern-based problems have initiated to be developed. Thanks to their ability to self-learn patterns in data, ML algorithms can predict the compressive strength of cementitious systems with high accuracy, depending on variables such as mix parameters and curing time. Many studies in literature have successfully modeled compressive strength for different types of cementitious system using artificial neural networks (ANN), support vector machines (SVM), random forests (RF), and various ensemble learning methods. These models offer lower error values and

higher generalizability than traditional methods, making them a powerful tool for predicting compressive strength. In particular, ensemble learning approaches such as boosting and bagging, where multiple weak learners are combined to form a robust model, have been highlighted in various studies in the literature as superior to individual models in terms of accuracy and stability [107, 152, 153].

In recent years, various studies using machine learning on the prediction of compressive strength are summarized comprehensively in Table 5.7. These current studies in the literature reveal which models offer the best predictive performance by comparing different algorithms and datasets. The datasets used in the studies are generally compiled from literature, and the number of samples varies between 84 and 3232. The inputs are generally similar (they include the components of the cementitious system), while the output is always the compressive strength. The machine learning algorithms used are quite diverse; many methods, such as support vector regression (SVR), random forest (RF), artificial neural networks (ANN), deep neural networks (DNN), gradient boosting (GB, XGB, GTB), have been tried. These comparisons show that ensemble methods and models with hyperparameter optimization provide high accuracy. For example, Kashifi et al. (2024) tested the XGBoost algorithm on the largest dataset with 3232 samples and showed the best performance with $R^2 = 0.952$ and $RMSE = 4.88$. This table clearly demonstrates the development, diversity, and performance levels of machine learning methods in compressive strength prediction.

Table 5.7 Literature overview of machine learning studies on compressive strength prediction

Study	ML algorithms	Inputs	Dataset source/size	Best performing model/ Testing Result
Al-Jamimi et al., 2022 [107]	SVM and the genetic algorithm (hybrid model)	Cement, water, silica fume, fly ash, coarse and fine aggregate, and age	Literature-based dataset/ 108 samples	SVM and the genetic algorithm (hybrid model) / $R^2 = 0.992$, $RMSE = 0.002$

Choi et al., 2023 [154]	SVR, RF, DNN	Cement, water, coarse and fine aggregate, fly ash, blast furnace slag, curing temperature, and humidity	Ready-mix plant data, South Korea/ 775 samples	DNN with 3 hidden layers and 64 units (neurons) per layer/ MAE = 1.67, MSE = 5.31
Aslam and Shabab, 2024 [96]	GEP, ANN, RF, SVR, ANFIS, GPR, GB, XGB, AB, KNN, BR	Cement, water, fly ash, slag, silica fume, lime powder, calcined clay, coarse and fine aggregate, superplasticizer	Literature-based dataset/ 1288 samples	XGB / $R^2= 0.888$, RMSE: 5.43, MAE= 3.98
Ansari et al., 2024 [152]	ANN, SVR, DT (with hyperparameter tuning)	Blast furnace slag to binder ratio, age, and ultrasonic pulse velocity	Literature-based dataset/ 84 samples	ANN with 2 hidden layers, 10 neurons per layer / $R^2=0.95$, RMSE=2.60, MAE=2.12
Jubori et al., 2024 [155]	ANN (Levenberg-Marquardt, Bayesian Regularization)	Cement, water/binder, coarse and fine aggregate, fly ash, silica fume, slag, superplasticizer	Literature-based dataset/ 1013 samples	ANN with 1 hidden layer, 15 neurons (Bayesian Regularization) / $R^2 = 0.959$, RMSE=5.1
Kashifi et al., 2024 [156]	LR, DT, RF, DNN, XGB(Bayesian optimization used)	Cement, fly ash, slag, water, superplasticizer, coarse and fine aggregate, and age	Literature-based dataset/ 3232 samples	XGB / $R^2=0.952$, RMSE=4.88, MAE =3.24,
Murthy et al., 2024 [157]	ANN, GTB, MARS	Cement, blast furnace slag, fly ash, superplasticizer, water, coarse and fine aggregate	Literature-based dataset/ 1030 samples	GTB/ $R^2=0.867$, RMSE=5.38, MAE=3.58
Khan et al., 2025 [158]	Hybrid SVR	cement, fly ash, silica fume, slag, lime powder, calcined clay, water/binder ratio, superplasticizer, coarse and fine aggregates	Literature-based dataset/ 1287 samples	SVR-firefly algorithm/ $R^2=0.93$, RMSE=7.44 , MAE=5.54

Prasad et al., 2025 [159]	LightGBM and ANN Fusion	Cement, water, slag, fly ash, superplasticizer, coarse aggregate, fine aggregate, age	Literature-based dataset/ 1030 samples	ANN fusion/ $R^2 = 0.95$, RMSE=3.97, MAE=3.17
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*SVR: support vector regression, RF: random forest, DNN: deep neural network, GEP: gene expression programming, ANN: artificial neural network, RF: random forest, ANFIS: adaptive neuro-fuzzy inference system, optimized GPR: Gaussian process regression, GB: gradient boost, XGB: extreme gradient boost, AB: Ada boost, KNN: k-nearest neighbor, BR: bagging regressor, DT: decision trees, LR: linear regression, GTB: gradient tree boosting, MARS: multivariate adaptive regression splines

This study utilizes various conventional and ensemble-based machine learning algorithms to predict the compressive strength of superplasticized blended cement pastes. During the compressive strength results analysis, a total of 6 inputs and 4 different outputs were evaluated. The input variables are OPC content (%mass), SP type, SP content (%), SCM (μm), water/binder ratio, and SCM $\text{SiO}_2 + \text{Al}_2\text{O}_3$ content (%). The outputs are compressive strength at 2, 7, 28, and 90 days (MPa). The results of three statistical parameters – RMSE, MPa, R^2 , unitless, and MAE, MPa - used to evaluate all models are presented in Table 5.8 for compressive strength at 3, 7, 28, and 90 days. Lower values for RMSE and MAE and higher values for R^2 generally indicate better model performance. For all regression classes in MATLAB software (given in section 4.4), the results of the model that gives the two best results of different classes are given. Models for all outputs (compressive strength at 3, 7, 28, and 90 days) were analyzed as a 20/80 split test/training set. Table 5.8 presents a comparison of the prediction results for both training and test results of the two best-performing models for each output of compressive strength.

The highest accuracy in 2-day compressive strength predictions was achieved with the interactions linear model. This model showed highly successful results on the test data, with $R^2 = 0.90$, RMSE = 1.69, and MAE = 1.33. Because strength development at early ages is generally influenced by key components such as cement content and water/binder ratio, the system behavior exhibits a structure suitable for linear models. Furthermore, the inclusion of interaction terms in the model allowed for the capture of limited nonlinear interactions between variables. While the Boosted Tree model produced similarly accurate results, the lower test errors of the linear model demonstrate the limited

complexity of the early-age strength development. The cementitious system complexity started to increase in the 7-day compressive strength predictions, and linear models were found to be inadequate. Exponential GPR and Medium Gaussian SVM models exhibited similar performance profiles, with $R^2 = 0.80$ and 0.79 , respectively, for the test data. The RMSE and MAE values are also quite similar between the two models. These results indicate that the processes affecting strength development in this age (e.g., partial pozzolanic reactions and C–S–H development) involve nonlinear effects and cannot be fully represented by linear models. The high performance of kernel-based methods such as GPR and SVM during this period indicates that they can better represent the complexity of the system. For 28-day compressive strength predictions, the Wide NN and Exponential GPR models achieved similar accuracy levels on the test data ($R^2 = 0.78$ and 0.75 , respectively). However, both models produced high RMSE and MAE values on the training set, indicating a risk of overfitting, particularly in the neural network model. The factors determining compressive strength at this age consist not only of the principal components but also of more complex, multidimensional effects such as pozzolanic reactions, microstructural densification, and porosity. Therefore, more flexible, nonlinear learning models are needed to model these processes. In 90-day compressive strength predictions, the Trilayered NN and Exponential GPR models demonstrated similarly high performance; the test R^2 value for both models were 0.88 , and the RMSE and MAE values were quite similar. The primary factors determining strength at this age are advanced pozzolanic reactions, microstructural densification, and phase changes caused by hydration products at later ages. These complex and hidden patterns, which cannot be described by classical statistical methods, can be more effectively represented by models with flexible learning capabilities, such as neural networks and GPR. The GPR model's ability to consider not only the mean value but also uncertainties in the prediction process are a significant advantage that increases its generalizability in such multivariate systems.

Generally, linear models provide sufficient performance at early ages, but as the system ages, its complexity increases, and nonlinear models become necessary. The importance of GPR and neural network models, particularly in 28- and 90-day strength predictions, demonstrates their ability to effectively represent the nonlinear, multivariate nature of hydration and PC-SCM-SP interactions at late ages. This highlights the need to use different models for strength predictions depending on age.

In this study, various machine learning models developed to predict compressive strength at different ages (2, 7, 28, and 90 days) were evaluated using test data, and the results were compared with recent studies reported in literature. Table 5.7, which shows as a literature summary, reveals the existence of studies conducted in recent years with numerous different algorithms and datasets, demonstrating the increasing interest in compressive strength prediction. The models used in this study appear to yield results similar to or better than most literature studies, particularly with low RMSE and high R^2 values. For example, the Interactions Linear model's $RMS=1.69$ and $R^2=0.90$ for 2-day is successful in terms of early age compressive strength estimation and is close to the accuracy achieved by many studies at 28 days. The $RMSE \approx 2.60-2.63$ and $R^2 \approx 0.79-0.80$ values obtained with the Exponential GPR and Medium Gaussian SVM models for 7 days are quite similar to the $RMSE = 2.60$ and $MAE = 2.12$ results reported by Ansari et al [152]. The Wide Neural Network model for 28-day performed better than the values frequently encountered in the literature, with $RMSE=2.88$ and $MAE=2.15$ on the test set. For example, in the study by Jubori et al. (2024), $RMSE = 5.1$ was obtained with the ANN model, while this study achieved much lower error values with an ANN model [155]. Furthermore, the Trilayered Neural Network model used for 90-day yielded robust results with $RMSE = 3.05$ and $R^2=0.88$, values similar to those reported by Murthy et al. (2024), who reported $R^2=0.86$, $RMSE=5.38$, and $MAE=3.58$, significantly outperforming the values reported by the authors [157].

Overall, the models developed in this study offer a more comprehensive and detailed approach than models developed separately for different ages, which generally focus solely on 28-day compressive strength estimation. Furthermore, results were obtained that are comparable to the performance of XGBoost, ANN, and SVR-based models frequently used in literature. The results demonstrate that the models used are reliable in terms of both accuracy and generalization and can be used effectively in compressive strength estimation. Besides, the dataset used in this study is based on original, experimentally obtained real data, not on compiled data as is often found in literature. This not only enabled a more reliable and controlled modeling process but also significantly increased the scientific contribution and practical value of the study. The results presented here were obtained without hyperparameter optimization. The final performances of the models after detailed hyperparameter tuning will be presented in detail in Section 5.4.2. This means that the current results do not actually reflect the best

versions of the models, and therefore, further improved results will be obtained in the following sections.

Table 5.8 Performance of selected models in predicting compressive strength at 2, 7, 28 and 90 days

Output	Model		RMSE	R ²	MAE
@2 day	Interactions Linear	Training*	3.65	0.59	2.59
		Test	1.69	0.90	1.33
	Boosted Tree	Training*	3.18	0.69	2.32
		Test	1.77	0.89	1.35
@7 day	Exponential GPR	Training*	3.33	0.79	2.56
		Test	2.60	0.80	1.93
	Medium Gaussian SVM	Training*	3.36	0.78	2.53
		Test	2.63	0.79	1.79
@28 day	Wide NN	Training*	5.56	0.49	4.02
		Test	2.88	0.78	2.15
	Exponential GPR	Training*	5.01	0.58	4.04
		Test	3.09	0.75	2.39
@90 day	Trilayered NN	Training*	5.16	0.64	4.00
		Test	3.05	0.88	2.36
	Exponential GPR	Training*	4.73	0.70	3.88
		Test	3.06	0.88	2.71

**With 10-fold cross-validation*

Figure 5.21, Figure 5.22, Figure 5.23, and Figure 5.24 show scatter plots of actual and predicted compressive strength values for 2, 7, 28, and 90 days, respectively. These

graphs visually demonstrate the overall performance of the models used in predicting the compressive strength of cement pastes at different ages (2, 7, 28, and 90 days). The distribution between actual and predicted values is concentrated around the linear reference line ($y = x$), indicating that all models generally exhibit good predictive accuracy. The proximity of the points to the line is consistent with the high R^2 values and low RMSE/MAE values, indicating that the predicted results largely agree with the actual values. These scatter plots confirm model performance both quantitatively and qualitatively, and also demonstrate that the algorithms used can successfully predict compressive strengths at different ages. This is an important finding as it shows that the developed models can be used safely in strength prediction and that they give consistent results at different ages.

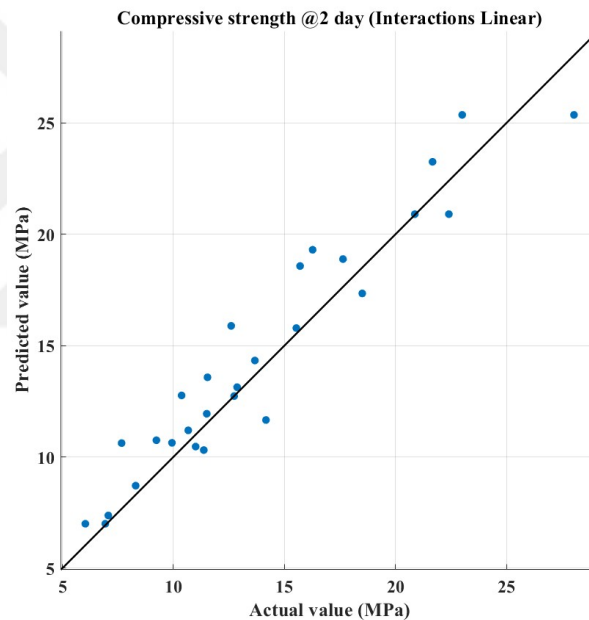


Figure 5.21 Actual vs. predicted compressive strength values at 2 days for the interactions linear model

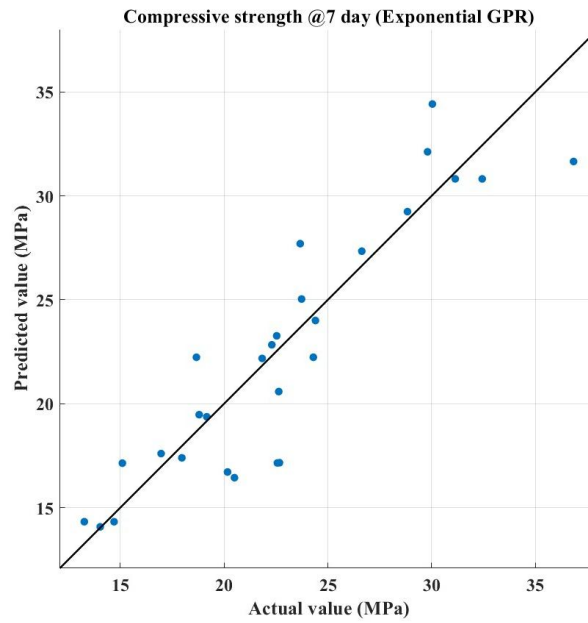


Figure 5.22 Actual vs. predicted compressive strength values at 7 days for the Exponential Gaussian Regression model

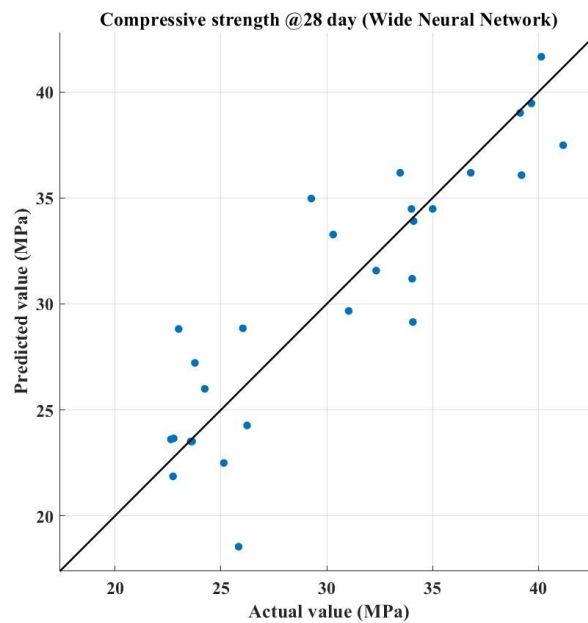


Figure 5.23 Actual vs. predicted compressive strength values at 28 days for the Wide Neural Network model

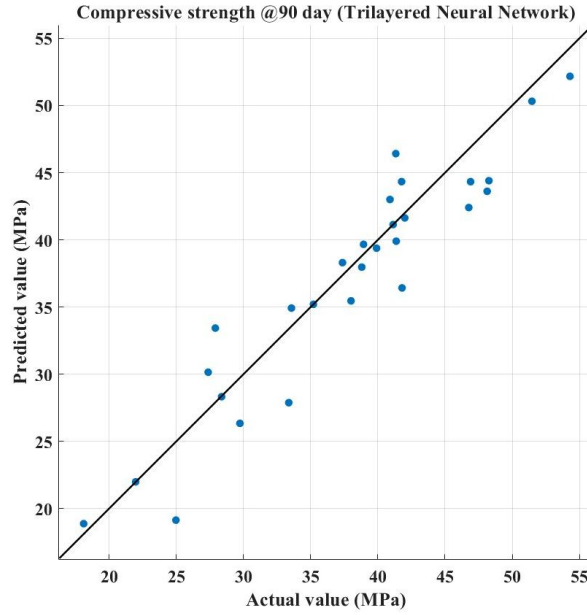


Figure 5.24 Actual vs. predicted compressive strength values at 90 days for the Trilayered Neural Network model

5.4.2 Hyperparameter Tuning Analysis

The success of machine learning models depends heavily on the chosen hyperparameters. Therefore, determining the most appropriate hyperparameters to maximize a model's performance on a specific task is critical. Hyperparameter tuning aims to increase the generalizability of a model to diverse datasets by limiting overfitting. In other words, determining the ideal hyperparameter combinations is essential to improving model accuracy. Because manual tuning hyperparameters can be time-consuming and inefficient, various methods have been developed to automate this process. Grid search, random search, successive halving, and Bayesian optimization are among the approaches used for this purpose [160]. Random search (RS) and grid search (GS) are the most commonly used hyperparameter configuration techniques. As the parameter space expands, the computational resources and time required for GS also increase. As the parameter size expands, the computational effort required for grid search increases exponentially. RS does not utilize the entire hyperparameter space, but creates a parameter subspace using partial parameter combinations to search within the subspace. This increases computational speed while also ensuring search accuracy [161].

In this study, random search optimization was used due to the long runtime and large number of models required by the grid search optimization method. The Random Search (RS) algorithm offers an approach based on random combinations in the parameter space for tuning model hyperparameters. In this method, a large number of possible combinations are randomly selected and tested using a specific function, and the parameter values that provide the best performance are determined. Evaluating parameters without observing to fixed patterns allows the RS algorithm to scan a wider search space than the Grid Search method. This increases the likelihood of finding more effective parameter combinations, especially in complex models. Furthermore, RS stands out as a time-efficient method because it can produce results more quickly on lower-dimensional datasets [162].

Single model providing the highest accuracy were selected for each dataset in regression analyses performed for isothermal calorimetry, thermal analysis, and compressive strength data. If the selected model was nonlinear and suitable for hyperparameter tuning, hyperparameter optimization was performed for that model. The relevant results are presented in detail in this section. The hyperparameter tuning process varies depending on the model structure used. For example, the parameters optimized for the GPR (Gaussian Process Regression) model differ from those tuned for the Artificial Neural Network (NN); therefore, optimizations were performed separately, considering the parameter space specific to each model's internal structure. This approach aims to maximize the potential performance of each model and increase the reliability of the obtained results.

The tuned hyperparameter values for the isothermal calorimetry dataset are presented in Table 5.9. Hyperparameter optimization was performed using a Random Search strategy, with 100 iterations applied to each model configuration. The process focused on tuning several critical parameters for both Neural Network (NN) and Gaussian Process Regression (GPR) models. Specifically, for NN models, the number of hidden layers, the distribution of nodes, and activation functions were adjusted — for instance, reducing the number of hidden layers from three to two and replacing ReLU activations with Sigmoid functions. In parallel, GPR models originally employing constant basis functions and exponential kernels were optimized by substituting alternative configurations such as zero or linear basis functions and more flexible, Nonisotropic kernel types including Matern 3/2 and Rational Quadratic. Although the Cubic SVM

model results for the Total heat at 72 h output are presented in Table 5.5, this model was excluded from the hyperparameter optimization process due to its poor performance. Given its significantly lower predictive accuracy compared to other models, further tuning was not pursued as it was unlikely to yield meaningful improvements. Although the initial performance of the Cubic SVM model for the Total heat at 72 h output was satisfactory, hyperparameter optimization led to a substantial decline in test performance. This deterioration may be attributed to the model's sensitivity to parameter changes and its tendency to overfit when complex kernel configurations are introduced. The optimization process, rather than enhancing generalization, may have disrupted the balance between training accuracy and test robustness. Given this outcome, further hyperparameter tuning of the SVM model was not considered practical.

Table 5.9 Summary of hyperparameter tuned values for isothermal calorimetry dataset

Output	Model	Hyperparameter	Default value	Optimized value
Onset time	NN	Hidden layer	3	2
		Node number	10, 10, 10	17, 133
		Activation function	ReLU	Sigmoid
	GPR	Basic function	Constant	Zero
		Kernel function	Exponential	Nonisotropic Matern 3/2
Onset heat	NN	Hidden layer	3	2
		Node number	10, 10, 10	48, 33
		Activation function	ReLU	Sigmoid
	GPR	Basic function	Constant	Linear
		Kernel function	Exponential	Nonisotropic Rational Quadratic

Induction period	NN	Hidden layer	3	2
		Node number	10, 10, 10	56, 175
		Activation function	ReLU	Sigmoid
	GPR	Basic function	Constant	Zero
		Kernel function	Exponential	Nonisotropic Matern 3/2
Total heat at 72 h	GPR	Basic function	Constant	Zero
		Kernel function	Exponential	Nonisotropic Rational Quadratic

Table 5.10 demonstrates the impact of hyperparameter tuning on the isothermal calorimetry dataset on model performance. The results demonstrate that overall, successful improvements were achieved on the training data. After optimization, significant decreases were observed in RMSE and MAE values during the training phase, while R^2 values increased. This demonstrates that the adjusted parameters increased the learning capacity of the models and enabled them to capture data patterns with lower error. However, the impact of optimization on the test data was not consistent across all models. After optimization, there were slight, positive improvements in test performance in the onset Time and onset Heat outputs. For example, the GPR model demonstrated balanced generalization success by reducing MAE and RMSE on test data while maintaining the R^2 value.

Conversely, the NN model optimized for the induction period output showed a significant decrease in test accuracy and an increase in error values. This suggests that hyperparameter tuning causes the model to overfit, weakening its ability to generalize to the test data by overfitting the training data. While hyperparameter optimization often improves model performance, it has been noted that it can negatively impact test performance, especially with complex models or when the dataset is limited or incomplete. Indeed, Zhang et al. clearly demonstrated this by stating that the hyperparameter tuning process can be quite time-consuming and that the results obtained are highly dependent on the quality of the dataset [163]. Additionally, different machine learning models exhibit varying sensitivity to hyperparameter changes. Table 5.9 shows

that GPR models generally exhibit a more stable structure, whereas more complex models like NNs are more sensitive to parameter changes, thus negatively impacting generalization performance. Indeed, the literature indicates that complex models like artificial neural networks are highly sensitive to hyperparameters such as the number of layers and neurons, and that incorrect tuning of these parameters can easily lead to overfitting and underfitting. Therefore, as model complexity increases, the impact of hyperparameter tuning on generalization performance becomes more critical, causing some models to be more susceptible to optimization [164].

Therefore, while hyperparameter optimization offers the potential to increase model performance, it does not yield equally positive results for every model and output. Factors such as the model structure, the characteristics of the dataset, and the appropriateness of parameter ranges directly determine the efficiency of optimization. Therefore, the hyperparameter tuning should be carefully conducted, considering not only training accuracy but also test performance; each output should be evaluated individually.

Table 5.10 Summary of hyperparameter tuning results using Random Search for the isothermal calorimetry dataset

Output	Model		RMSE	R ²	MAE
Onset time	Trilayered NN	Training	102.18	0.70	43.29
		Test	50.05	0.90	21.93
	Optimized NN	Training	93.18	0.75	38.36
		Test	50.93	0.89	21.75
	Exponential GPR	Training	94.0	0.74	39.68
		Test	53.33	0.88	22.60
	Optimized GPR	Training	83.70	0.80	31.5
		Test	51.00	0.89	19.96
Onset heat	Trilayered NN	Training	0.22	0.63	0.13
		Test	0.07	0.97	0.04

	Optimized NN	Training	0.13	0.88	0.09
		Test	0.10	0.93	0.07
	Exponential GPR	Training	0.19	0.73	0.12
		Test	0.07	0.96	0.05
	Optimized GPR	Training	0.12	0.89	0.07
		Test	0.07	0.96	0.05
Induction period	Trilayered NN	Training	106.37	0.66	51.25
		Test	44.21	0.95	24.05
	Optimized NN	Training	96.41	0.72	49.70
		Test	104.16	0.70	46.96
	Exponential GPR	Training	92.12	0.74	49.18
		Test	63.11	0.89	33.53
	Optimized GPR	Training	68.31	0.86	38.72
		Test	59.04	0.90	34.08
Total heat at 72 h	Exponential GPR	Training	18.82	0.69	13.17
		Test	10.12	0.93	7.57
	Optimized GPR	Training	15.7	0.79	10.76
		Test	9.78	0.94	7.55

Table 5.11 presents the default and optimized hyperparameter values for the GPR and NN models used in hyperparameter tuning applied to the thermal analysis dataset. Additionally, Table 5.12 shows a comparison of model performance before and after hyperparameter tuning on training and test data. An examination of Tables 5.11 and 5.12 clearly demonstrates that the impact of hyperparameter optimization on model performance varies depending on the model type and the predicted output. For the 3-day relative calcium hydroxide (CH) content output, hyperparameter tuning yielded to the

training data in both the NN and GPR models had positive performance effects. Decreases in RMSE and MAE values and increases in R^2 values were observed in the training sets of the optimized models. In particular, increasing the number of layers and neurons in the NN model and changing the activation function increased the model's learning capacity and provided a better fit to the training data with lower errors. However, when examining the test data, it is observed that the optimization had limited impact for both models; test errors increased in the GPR model, while the NN model only achieved a slight improvement in MAE. Similarly, models optimized for 28-day CH content output yielded better results during the training; however, no significant improvement was achieved in test performance, and some metrics even deteriorated. For example, test RMSE and MAE values increased in the optimized GPR model, suggesting that the hyperparameter tuning caused overfitting to the training data. Similarly, while training accuracy increased, test accuracy decreased in the NN model, weakening the model's generalization ability.

These results suggest that while hyperparameter tuning improves learning quality on training data, this increase may not be directly and consistently reflected in test performance. Similarly, the decrease in test performance observed here can be explained by overfitting, model complexity, and data structure factors discussed in the isothermal analysis results. Especially when model complexity increases, the risk of overfitting must be considered, and the hyperparameter tuning must be carefully evaluated not only against training performance metrics but also against test performance.

Table 5.11 Summary of hyperparameter tuned values for thermal analysis dataset

Output	Model	Hyperparameter	Default value	Optimized value
Relative CH content @3 day	GPR	Basic function	Constant	Zero
		Kernel function	Exponential	Nonisotropic Rational Quadratic
	NN	Hidden layer	1	2
		Node number	25	217, 92
		Activation function	ReLU	Tanh

Relative CH content @28 day	GPR	Basic function	Constant	Zero
		Kernel function	Exponential	Nonisotropic Rational Quadratic
	NN	Hidden layer	2	2
		Node number	10, 10	255, 5
		Activation function	ReLU	ReLU

Table 5.12 Summary of hyperparameter tuning results using Random Search for the thermal analysis dataset

Output	Model		RMSE	R²	MAE
Relative CH content @3 day	Exponential GPR	Training	5.94	0.89	4.64
		Test	3.84	0.94	2.87
	Optimized GPR	Training	5.72	0.90	4.43
		Test	4.60	0.92	3.47
	Medium NN	Training	7.37	0.83	5.56
		Test	4.39	0.92	3.44
	Optimized NN	Training	5.69	0.90	4.39
		Test	4.56	0.92	3.17
	Exponential GPR	Training	8.26	0.89	6.00
		Test	4.90	0.96	3.95
Relative CH content @28 day	Optimized GPR	Training	7.54	0.91	5.58
		Test	5.63	0.95	4.67
	Bilayered NN	Training	9.97	0.85	7.44
		Test	4.90	0.96	3.80

	Optimized NN	Training	8.11	0.90	5.94
		Test	6.46	0.93	5.12

Table 5.13 and Table 5.14 show the hyperparameter tuning performed for different machine learning models on the compressive strength dataset, and the effects of these tuning on model performance, respectively. Table 5.13 summarizes the default and optimized hyperparameter values for the models used for four different ages. Table 5.14 presents a comparison of the error (RMSE, MAE) and R^2 values for these models on the training and test data.

The Boosted Tree model performed the best for 3-day compressive strength predictions, which is why the parameters of the Ensemble models were optimized. While the hyperparameter tuning resulted in minor improvements in the errors on the training data, the test performance remained almost constant. This indicates that the model already has a stable structure and that model performance metrics cannot be improved further with optimization. For the 7-day compressive strength predictions, GPR and SVM models were used, and both models observed improvements on the training data after hyperparameter tuning. However, no significant improvement was achieved in test performance, and some metrics even experienced minor regressions. In particular, the RMSE and R^2 values in the GPR model decreased on the test data compared to the unoptimized version. This indicates that while training accuracy increased, generalization ability weakened, and a risk of overfitting occurred. Even with the kernel type changed in the SVM model, test performance did not improve. These results indicate that the effects of hyperparameter tuning to models with high hyperparameter sensitivity on the test data should be carefully monitored. For the 28-day compressive strength prediction, more extensive optimization was made to both the NN and GPR models. In the NN model, the number of layers was increased, the number of neurons was rearranged, and the activation function was changed. While these changes improved training performance, no significant increase in test performance was achieved. In fact, the test MAE value of the optimized NN model increased compared to the default model. In the GPR model, the kernel function was modified, and training accuracy increased, but the results on the test data remained largely stable. This situation once again highlights the need for a careful balance between training and test performance. The 90-day compressive strength predictions yield a more striking result than the other ages. While the optimized NN

model provided minor improvements on the training data, it suffered a significant performance loss on the test data, with a particularly noticeable increase in the MAE value. This suggests that the model overfitted the training data and weakened its generalization ability. In contrast, hyperparameter tuning to the GPR model produced better results on both the training and test data; the optimized GPR model reduced the error rate and maintained the explained variance constant on the test data. This demonstrates that GPR models have a more stable structure and can be more resilient to hyperparameter changes than NN models. Indeed, the underlying reasons for this difference have previously been observed on the isothermal dataset, where it has been observed that hyperparameter tuning, especially in models with complex structures (e.g., NN), can lead to overfitting, negatively impacting test performance.

Overall, these results demonstrate that hyperparameter tuning does not always improve test performance; in some cases, it can negatively impact generalization performance by overfitting the training data. Especially in complex models (e.g., neural networks), the model's sensitivity to the test data increases, and even small parameter changes can lead to significant performance instabilities. This is consistent with findings observed in isothermal and thermal analysis datasets. Therefore, hyperparameter tuning should focus not only on training performance but also on test performance; it should be carefully conducted, considering the complexity of the model and the characteristics of the dataset.

Table 5.13 Summary of hyperparameter tuned values for compressive strength dataset

Output	Model	Hyperparameter	Default value	Optimized value
@2 day	Ensemble Tree	Ensemble method	Boosted	LSBoost
		Minimum leaf size	8	13
		Number of learners	30	31
@7 day	GPR	Basic function	Constant	Constant

	SVM	Kernel function	Exponential	Nonisotropic Squared Exponential
		Kernel function	Gaussian	Quadratic
		Kernel Scale	3	3
@28 day	NN	Hidden layer	1	2
		Node number	100	130, 12
		Activation function	ReLU	Sigmoid
	GPR	Basic function	Constant	Constant
		Kernel function	Exponential	Nonisotropic Matern 3/2
@90 day	NN	Hidden layer	3	3
		Node number	10, 10, 10	20, 29, 19
		Activation function	ReLU	Sigmoid
	GPR	Basic function	Constant	Zero
		Kernel function	Exponential	Nonisotropic Matern 3/2

Table 5.14 Summary of hyperparameter tuning results using Random Search for the compressive strength dataset

Output	Model		RMSE	R ²	MAE
@2 day	Boosted Tree	Training	3.18	0.69	2.32
		Test	1.77	0.89	1.35
	Optimized Ensemble Tree	Training	3.09	0.70	2.25
		Test	1.83	0.89	1.36
@7 day	Exponential GPR	Training	3.33	0.79	2.56
		Test	2.60	0.80	1.93

@28 day	Optimized GPR	Training	2.96	0.83	2.20
		Test	2.84	0.76	2.01
	Medium Gaussian SVM	Training	3.36	0.78	2.53
		Test	2.63	0.79	1.79
	Optimized SVM	Training	3.43	0.77	2.53
		Test	2.78	0.77	1.94
	Wide NN	Training	5.56	0.49	4.02
		Test	2.88	0.78	2.15
	Optimized NN	Training	4.76	0.62	3.78
		Test	2.93	0.77	2.39
	Exponential GPR	Training	5.01	0.58	4.04
		Test	3.09	0.75	2.39
	Optimized GPR	Training	4.58	0.65	3.45
		Test	3.08	0.75	2.37
@90 day	Trilayered NN	Training	5.16	0.64	4.00
		Test	3.05	0.88	2.36
	Optimized NN	Training	4.91	0.68	3.94
		Test	3.72	0.82	13.88
	Exponential GPR	Training	4.73	0.70	3.88
		Test	3.06	0.88	2.71
	Optimized GPR	Training	4.16	0.77	3.27
		Test	3.67	0.82	2.95

5.4.3 Feature Ranking Using F-test Analysis

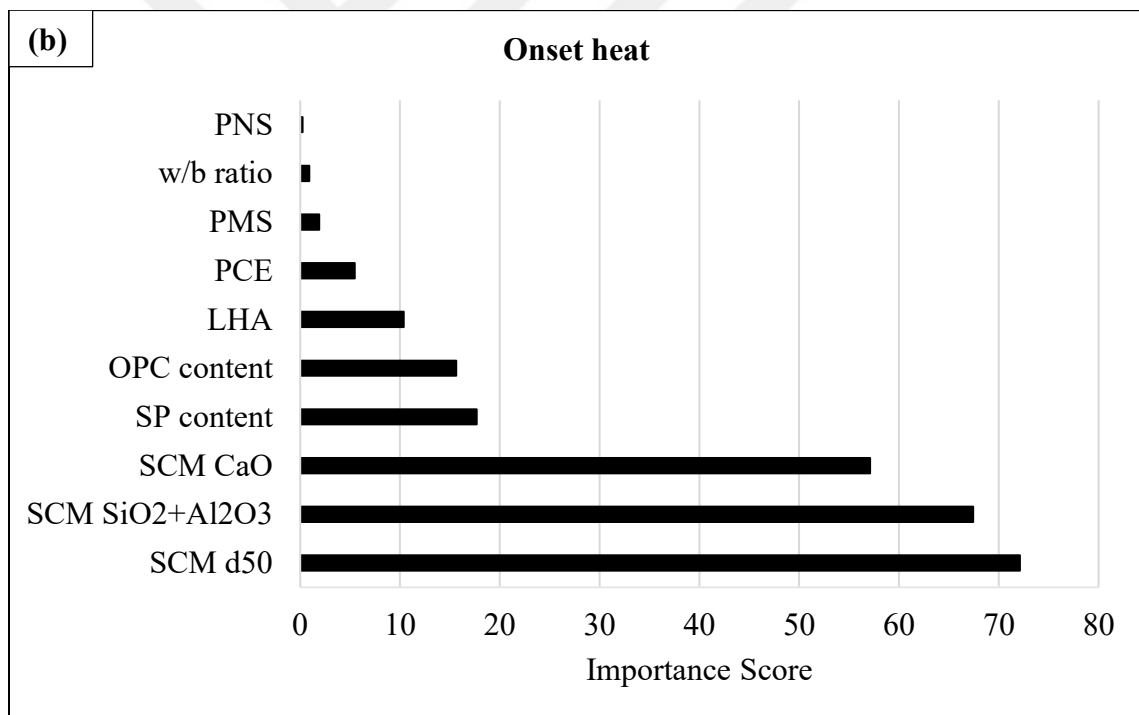
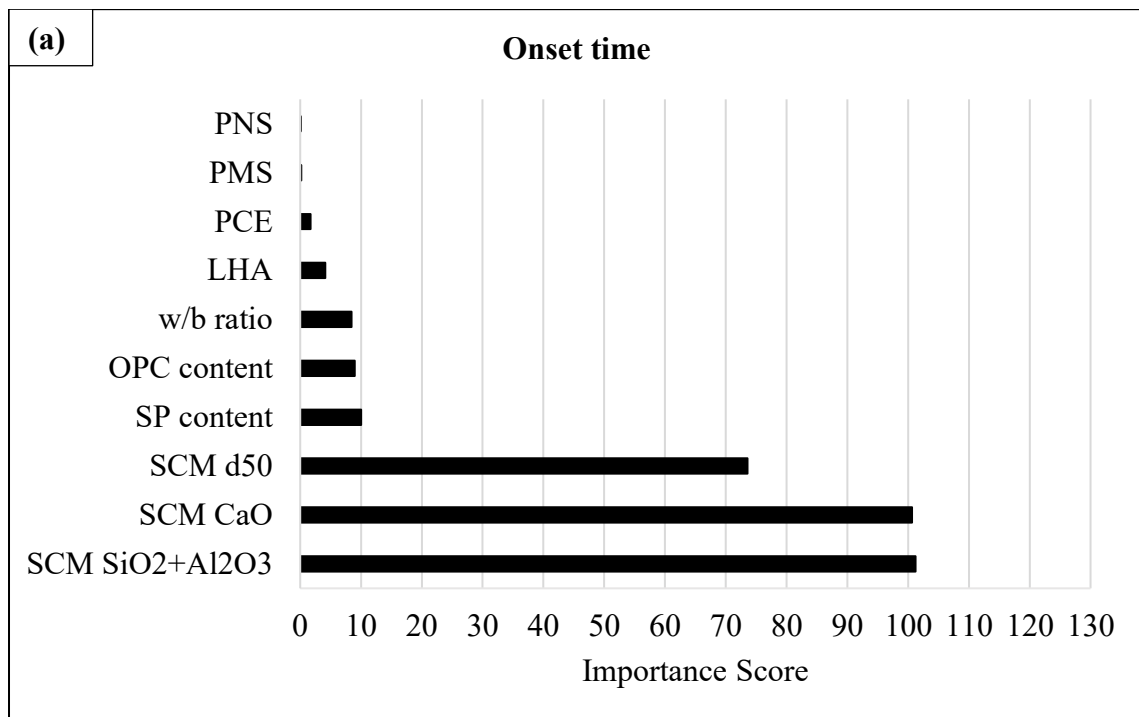
The success of machine learning models depends largely on the effects of the input variables used on the model. Therefore, determining which variables contribute most to the model's predictive ability is critical to both improving model interpretability and reducing unnecessary complexity. A feature ranking based on F-test analysis was performed for the datasets used in this study. The analysis evaluated the relative impact of each input variable on the outputs. This analysis was applied to all output variables of the isothermal calorimetry, thermal analysis, and compressive strength datasets, and the relative influence of the input parameters in each case was determined.

Figure 5.25 presents the results of the feature ranking analysis performed for isothermal calorimetry outputs. For each output parameter, the relative importance of variables belonging to four different regression problems was evaluated: (a) onset time, (b) onset heat, (c) induction period, and (d) total heat released at 72 h.

In the feature ranking for the onset time output, the most important variables were the SCM content parameters. In particular, the $\text{SiO}_2+\text{Al}_2\text{O}_3$ composition, CaO content, and SCM d_{50} value within the SCM stood out as the inputs providing the highest contribution to the model. This indicates that the chemical and physical properties of SCMs significantly influence the onset time. In contrast, superplasticizer types such as PNS, PMS, and PCE, as well as LHA and the water/binder ratio (w/b), are of lower importance and have a limited effect on the early reaction kinetics. A similar trend was observed for onset heat output, with the highest importance scores belonging to SCM d_{50} , $\text{SiO}_2+\text{Al}_2\text{O}_3$, and CaO contents. This indicates that the thermal energy released at an early age is largely related to the chemical composition and particle size of the SCM. In addition, the relative influence of SP content, w/b ratio, and LHA increased on this output. This suggests that not only SCMs but also the type and amount of superplasticizer may have an impact on the onset heat. The results obtained for the induction period output indicate that the physical and chemical properties of the SCM are as decisive as those for other outputs. At this stage, the highest significance was observed for SCM $\text{SiO}_2+\text{Al}_2\text{O}_3$, SCM CaO, and SCM d_{50} , respectively. This finding confirms that the induction period is largely related to the SCM type. SP content was of moderate importance at this stage, while superplasticizer types remained at a lower level. Finally, the analysis of the total heat released at 72 h yields results similar to the previous three outputs. While the SCM

$\text{SiO}_2 + \text{Al}_2\text{O}_3$ content stands out as the most important parameter, other SCM parameters are also influential, and it is noteworthy that inputs such OPC content and SP content have increased in importance. This result demonstrates that the total heat is sensitive not only to early hydration mechanisms but also to the binder content and the effects of superplasticizers.

Overall, feature ranking analyses performed on isothermal calorimeter outputs revealed that the physical properties of SCMs, along with their chemical composition, play a decisive role in the hydration kinetics. SCM chemical composition (e.g., CaO and $\text{SiO}_2 + \text{Al}_2\text{O}_3$ ratio) and particle size, in particular, stand out as highly influential variables on the rate and shape of early-age hydration kinetic reactions. These parameters directly influence both the soluble ion balance that drives C-S-H formation and the progression of pozzolanic reactions. Furthermore, the particle size distribution of SCMs and, consequently, SCM content (meaning of OPC content) shapes the reaction environment not only through chemical but also through physical mechanisms (e.g., the packing effect). Finer particles can increase the reaction surface area by filling voids in the cement matrix, facilitating the formation of hydration products and thus indirectly increasing the reactivity of the cementitious system. Additionally, superplasticizer (SP) parameters such as SP content and the type of SP used (e.g., PNS, PMS, PCE, or LHA) were observed to have significant effects on some outputs. These additives have indirect effects not only on workability but also on the ionic structure of the reaction medium and the timing of the hydration kinetics. Indeed, SPs adsorb onto cement and SCM surfaces, resulting in a more homogeneous distribution of particles and thus providing a larger surface area for hydration. On the other hand, some SP types can delay early-age hydration by interacting with calcium ions [165].



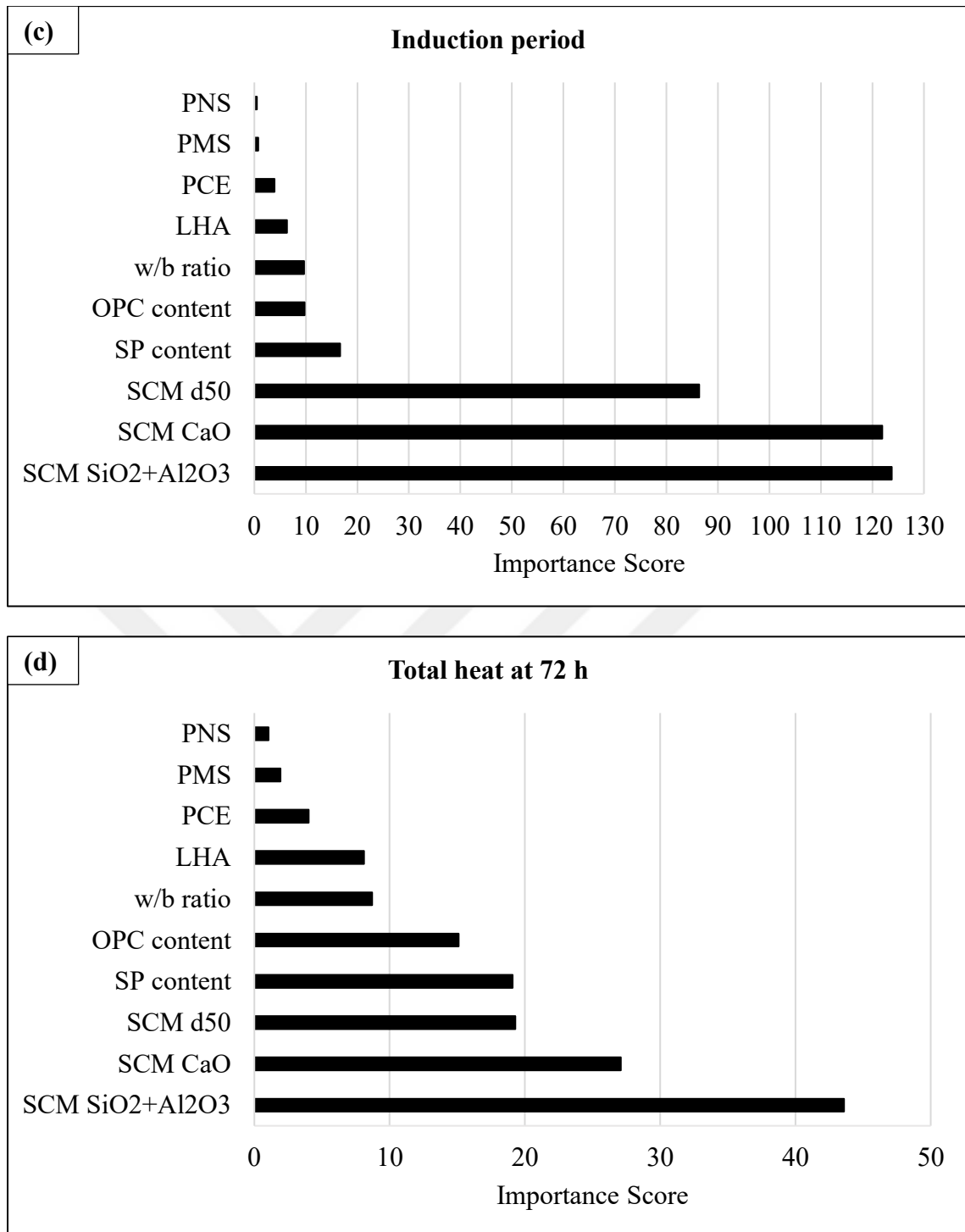


Figure 5.25 Feature ranking results for isothermal calorimetry outputs: (a) Onset time, (b) Onset heat, (c) Induction period, and (d) Total heat at 72 h

Figure 5.26 presents the results of the feature ranking analyses performed for the relative calcium hydroxide (CH) content of the thermal analysis outputs at 3 and 28 days. The graphs compare the relative impact of each parameter on the CH content based on their importance scores. When the results for the 3-day CH content are examined, it is

seen that the SP content has the highest importance score. The significant effect of superplasticizer (SP) content on the amount of CH (calcium hydroxide) can be explained by both physical dispersion mechanisms and chemical reaction processes. SPs adsorb onto the surfaces of cement and pozzolanic admixtures, increasing interparticle repulsive forces and inhibiting aggregation. This, in turn, allows particles to contact water over a larger surface area, increasing the rate of hydration at an early age and thus promoting CH production. On the other hand, some SP species can dissolve and affect the ionic structure in the system; in particular, they can interact with Ca^{2+} ions, altering the course of hydration, which directly affects the CH precipitation rate. Furthermore, the fact that SPs promote the reaction of pozzolanic admixtures with SCMs can reduce the amount of CH formed at later ages because pozzolanic reactions consume available CH and form secondary C-S-H gels. This dual effect makes SP content not only a improve fluidity but also important features affecting CH content. Therefore, SP dosage can directly determine the CH prediction performance of the model. This is followed by the SCM d_{50} , SCM $\text{SiO}_2+\text{Al}_2\text{O}_3$, and SCM CaO contents, respectively. This demonstrates that hydration reactions, especially at early ages, are closely related to both physical (particle size and surface effect) and chemical (pozzolanic reactivity) contributions. Indeed, CaO content increases C-S-H formation; SCM $\text{SiO}_2+\text{Al}_2\text{O}_3$ content contributes both to limited soluble reactive phases at early ages and forms the basis for pozzolanic reactions in later ages. When the 28-day CH content data is evaluated, SP content maintains the highest importance score, followed by SCM $\text{SiO}_2+\text{Al}_2\text{O}_3$, SCM CaO, SCM d_{50} , and OPC content. The notable point here is the increased importance of OPC content compared to day 3. This finding suggests that the effect of OPC content, and therefore SCM content, on the total hydration product amount becomes more pronounced at later ages. This may be attributed to pozzolanic reactions being more effective at later ages than at earlier ages.

When the two graphs are evaluated together, it is clearly seen that the SP content, chemical composition and particle size of SCM, and contributions are decisive for CH formation at both early and late ages. It can be said that these parameters play important roles in both the physical structure and chemical reaction mechanisms, directly affecting both the hydration rate and the amount of product formed. In this context, considering these variables, especially in modeling CH development, is critical for model performance.

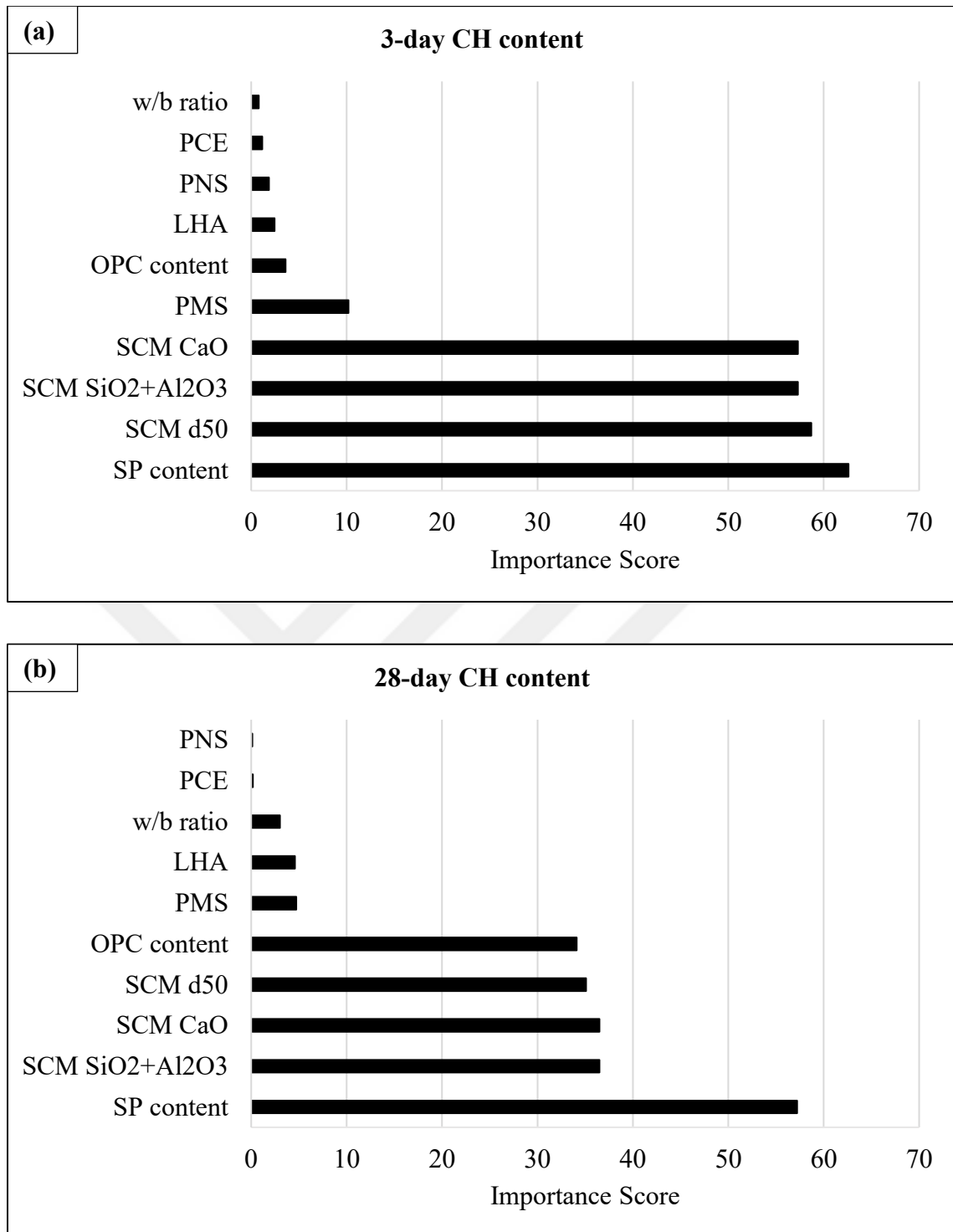


Figure 5.26 Feature ranking results for thermal analysis outputs: (a) Relative CH content at 3 days and (b) Relative CH content at 28 days

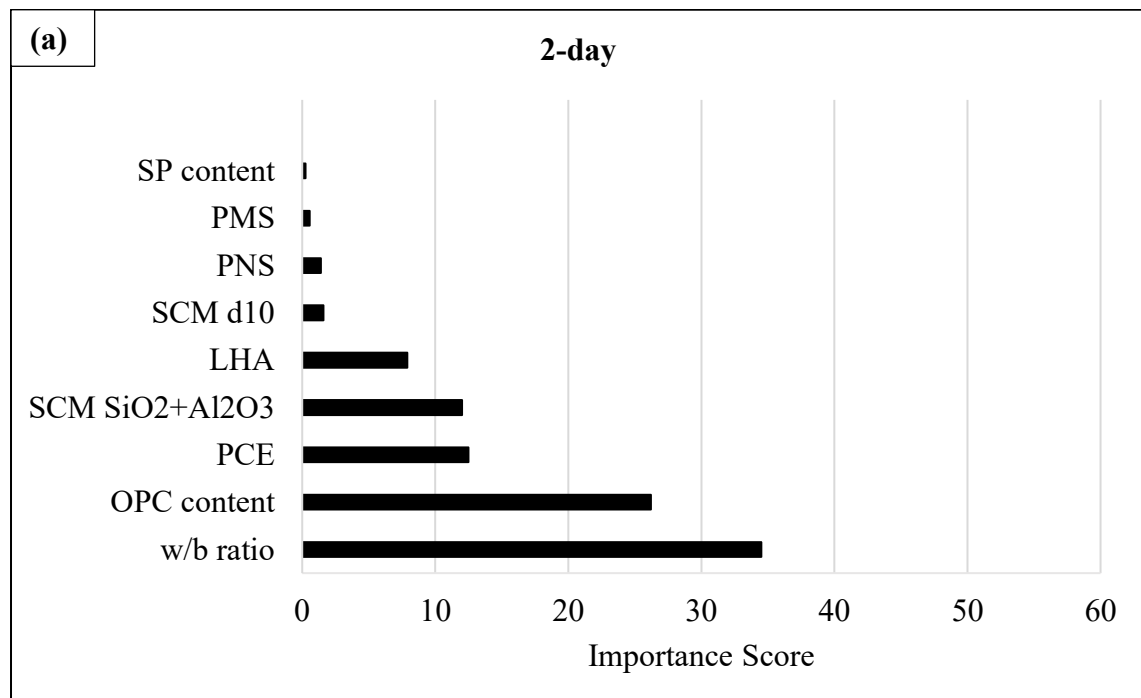
Figure 5.27 presents the results of the feature ranking analysis performed for compressive strength outputs. Within the scope of this analysis, independent regression problems were defined for four different ages: (a) 2 days, (b) 7 days, (c) 28 days, and (d)

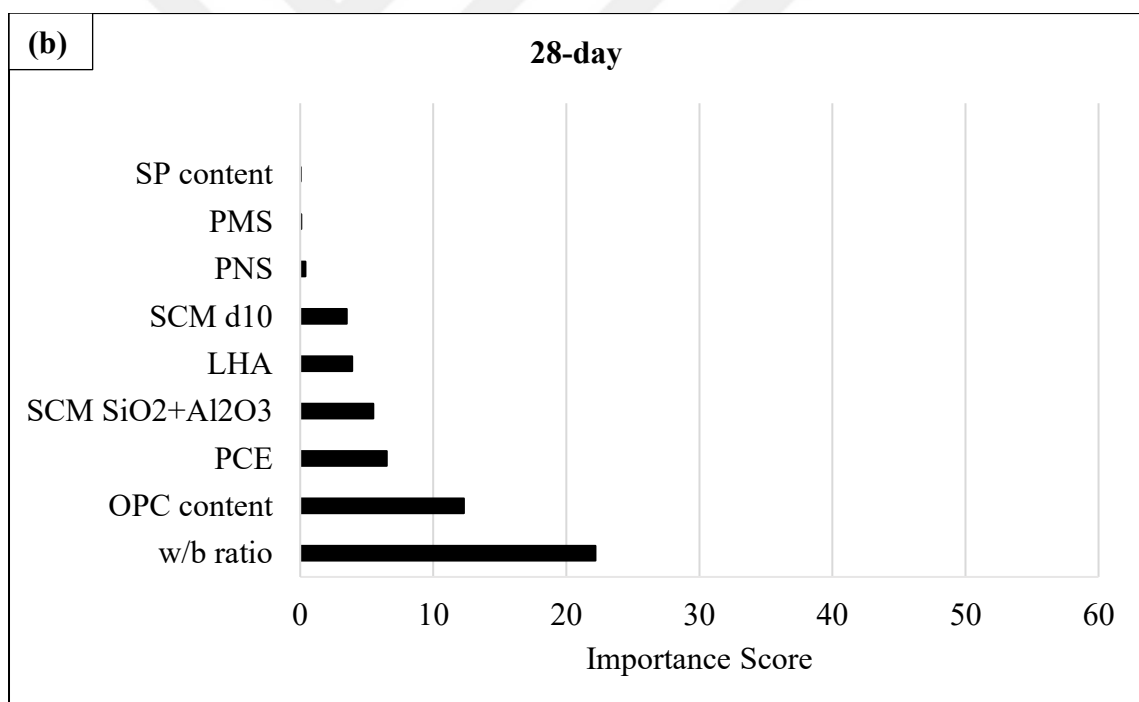
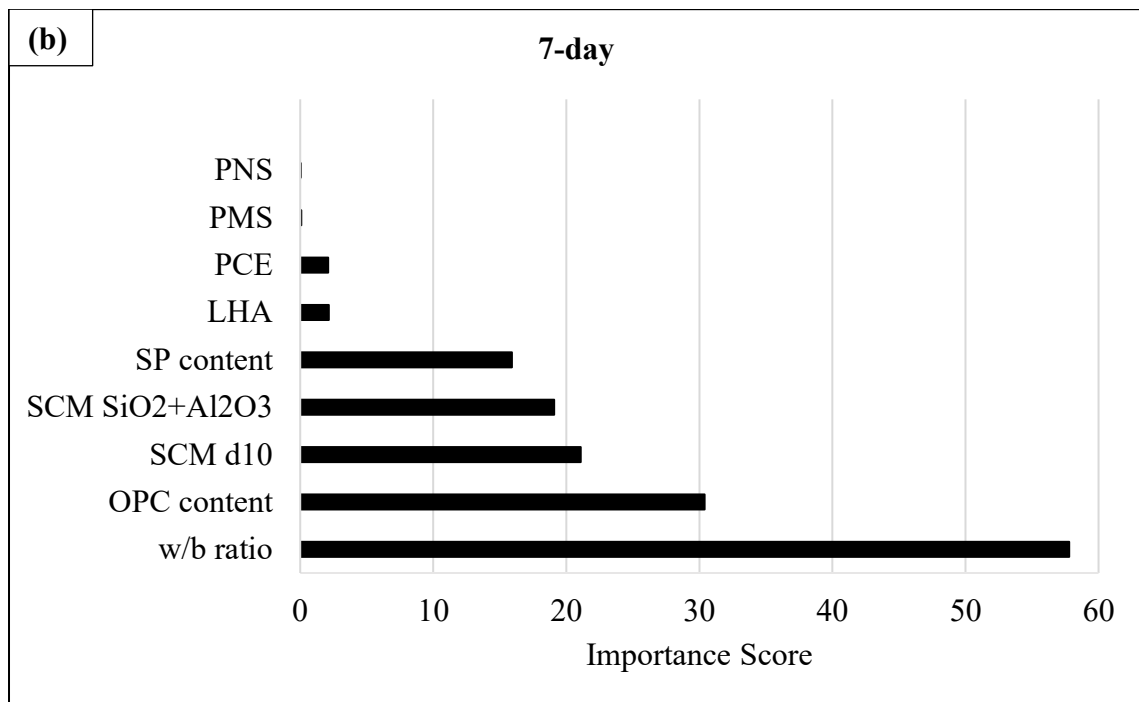
90 days. The relative importance levels of the inputs contributing to the model performance for each output variable were evaluated. These importance levels, determined using the F-test method, statistically demonstrate the impact of each input parameter on the relevant compressive strength output and allow for visualization of time-dependent effects.

The most significant parameters affecting compressive strength across all ages were the water/binder ratio (w/b) and OPC content. This demonstrates that compressive strength development is directly dependent on the degree of hydration and the amount of the binder phase. The water/binder ratio is a determining factor in matrix porosity and the formation of hydration products, with lower w/b ratios generally resulting in higher strength by creating a denser microstructure. Similarly, a change in the OPC content is a simultaneous change in the SCM content. This balance directly affects the reactivity profile of the binder system. OPC, particularly at early ages, provides a strong contribution to compressive strength development by producing high C-S-H and CH, while SCMs react more slowly, resulting in long-term strength and microstructure improvement. The sensitivity of the model in this direction indicates that strength development at early and late ages is directly dependent on the binder type, i.e., the amounts of OPC and SCM. The effect of SCM properties on compressive strength varies with age. Parameters such as SCM particle size (d_{10}), SCM $\text{SiO}_2 + \text{Al}_2\text{O}_3$, and CaO content are particularly high in importance at 7-day strength. This suggests that some SCMs contribute to the formation of hydration products at an early age, thus contributing to increased early strength. In the 28- and 90-day results, the effect of SCM is partially reduced, but not completely eliminated. This demonstrates that SCMs can affect strength not only through their physical filling effect but also through chemical reactivity and late reaction processes. The results regarding the type and amount of SP have a more complex effect. While the overall effect of SPs on compressive strength outputs appears low, it is noteworthy that some types, such as PCE and LHA, have relatively higher importance scores in compressive strength outputs. This suggests that superplasticizers can indirectly contribute to strength development not only through workability but also through hydration kinetics. Polycarboxylate-based admixtures, in particular, interact with cement and SCM surfaces to increase dispersion, which can lead to a more homogeneous microstructure development at early ages and, consequently, better strength performance. On the other hand, PCE and LHA superplasticizers can delay hydration reactions by

intensely adsorbing them onto cement and SCM surfaces at early ages and reducing ion concentrations in solution; this can limit early-age strength, particularly in systems with low degrees of hydration.

Consequently, compressive strength development is highly dependent on the amount of binder components, the hydration environment, and the physical parameters that determine the reaction kinetics. The w/b ratio and OPC content, in particular, are highly important at all ages and are among the indispensable input parameters for model performance. This demonstrates that classical features remain the primary determinants in compressive strength-focused studies, and regression analyses technically confirm this.





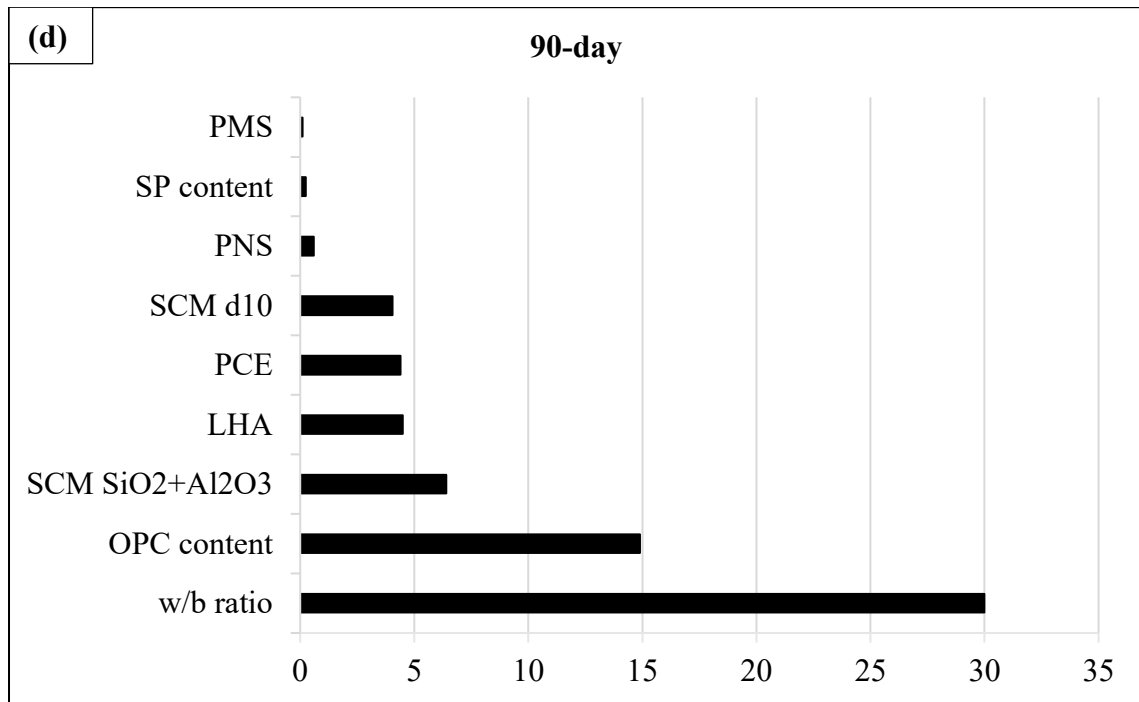


Figure 5.27 Feature ranking results for compressive strength outputs: (a) 2 days, (b) 7 days, (c) 28 days, and (d) 90 days

5.5 Multi-Criteria Compatibility Index (MCCI)

In the literature, the compatibility of PC–SCM–SP systems have typically been evaluated using a single performance indicator. However, such one-dimensional criteria fail to reflect the complex interactions of systems under multiple parameters. Therefore, a holistic assessment approach that simultaneously considers different criteria is needed. Such an approach will improve compatibility in cement-SCM-SP systems, enabling more efficient use of SCMs, thus reducing Portland cement usage and, consequently, reducing CO₂ emissions.

The Multi-Criteria Compatibility Index (MCCI) stands out as a unique contribution that addresses this gap in literature. The MCCI normalizes and weights various criteria into a single index, allowing it to simultaneously consider both early and long-term performance, as well as hydration kinetics, CH content, and compressive strength indicators. This approach allows for a multifaceted assessment of system compatibility, and the advantages and disadvantages of different mixtures can be systematically compared. This section presents the findings obtained from MCCI calculations performed on a synthetic mixture dataset generated using the developed regression models. First,

MCCI values were calculated for 1602 mixtures from 5000 candidate mixtures that met the physical and logical consistency criteria. Subsequently, the distribution of MCCI values and their relationships with various parameters (OPC content, superplasticizer ratio, particle size properties, and chemical composition) were examined in detail. Furthermore, the results obtained in terms of hydration behavior, CH content, and compressive strength development were interpreted, demonstrating the effectiveness of MCCI in reflecting system compatibility. Summary of distributions, trends according to MCCI intervals, and aggregated evaluations are presented in this section.

Table 5.15 presents the summary distribution of key parameters for a total of 1602 mixtures classified according to their MCCI ranges. The table includes the mixture numbers for each range, PC and SP contents, w/b ratio, SCM particle size properties (d_{50} and d_{10}), SCM chemical composition ($\text{SiO}_2 + \text{Al}_2\text{O}_3$ and CaO), and superplasticizer types (PCE, PMS, PNS, LHA). Thus, both compositional and performance-related indicators can be compared holistically under different compatibility index ranges. The parameters of the 1602 mixtures evaluated within the scope of the study vary within the following ranges: OPC content 45–90% (by mass of binder); SP content 0.00–1.54% (by mass of binder); SCM d_{10} 0.7–1.9 μm ; SCM d_{50} 4.0–10.8 μm ; SCM $\text{SiO}_2 + \text{Al}_2\text{O}_3$ 48.8–90.8 %; SCM CaO content 0.2–37.7%; and w/b ratio 0.40–0.50.

As seen in Table 5.15, the OPC content of the mixtures tends to decrease significantly as the MCCI ranges increase. In the low MCCI range (0.17–0.30), the average OPC content is approximately 70%, while in the very high MCCI range (>0.60), this value decreases to 60%. This indicates that the proportion of Portland cement in the binder composition decreases with increasing compatibility in the PC–SCM–SP systems. Consequently, higher MCCI values are associated with lower OPC contents and higher SCM ratios. While SCMs may limit early-age compressive strength, their lower heat of hydration, reduced CH formation, and long-term compatibility contribute to the overall MCCI evaluation.

Superplasticizer (SP) content appears to increase steadily and significantly in parallel with the increase in MCCI values. SP ratios remain quite limited (~ 0.37 – 0.47) in the low (0.17–0.30) and medium (0.30–0.45) MCCI ranges, while this value reaches ~ 0.70 in the high (0.45–0.60) range and reaches up to $\sim 1.10\%$ in the very high (0.60–0.75) range. This trend clearly demonstrates the critical and decisive role superplasticizers

play in improving system compatibility. High SP ratios, particularly when used in conjunction with low OPC contents (e.g., ~59% in the very high MCCI range), enhance the overall performance of the system by providing mixes with more homogeneous particle distribution, improved flowability, and superior workability. Therefore, increasing the SP is not only supportive but also a guiding factor in achieving high MCCI values. This result is consistent with findings reported in the literature that superplasticizer used with low water/binder (w/b) ratios support high strength development and microstructural density [166].

It is observed that quite similar average values are achieved for the particle size parameters of SCMs in all MCCI ranges. The d_{50} values remain constant in the range of ~7.4–7.5 μm , falling into the “medium” range, while the d_{10} values are at the level of ~1.3 μm , falling into the “fine” class. This finding shows that the main factor determining the compatibility index is not the particle size directly, but that maintaining a homogeneous and balanced distribution plays a critical role in the performance of the system. In other words, small changes in particle size do not have a decisive effect on MCCI; however, they are important as a complementary condition for the mixture to remain stable and balanced. Indeed, while it is stated in the literature that particle size can have an effect on SCM reactivity, it is emphasized that the main determinants in the appropriate fineness ranges are the chemical composition and rheological parameters (e.g., SP content, w/b ratio) [167]. The findings obtained in this study are also consistent with this view; it is revealed that the particle size is not a direct determinant in the MCCI evaluation, but a secondary and complementary parameter that maintains the balanced structure of the mixture.

Table 5.15 Summary of key parameters of 1602 mixtures classified by MCCI ranges

MCCI Range	Number of mixtures	OPC content	SP content	SCM d₁₀	SCM d₅₀	SCM SiO₂+Al₂O₃	SCM CaO	w/b ratio	PCE	PMS	PNS	LHA
0.17–0.30 (Low)	9	High (~70%)	Low (~0.37%)	Fine (~1.32)	Medium (~7.55)	High (~68%)	High (~26%)	High (~0.48)	0	0	3	6
0.30–0.45 (Medium)	659	High (~68%)	Low (~0.47%)	Fine (~1.37)	Medium (~7.4)	High (~74%)	High (~20%)	Medium (~0.45)	34	136	231	258
0.45–0.60 (High)	782	High (~65%)	Medium (~0.70%)	Fine (~1.35)	Medium (~7.4)	High (~75%)	Medium (~18%)	Medium (~0.44)	160	310	220	92
0.60–0.75 (Very High)	182	Medium (~59%)	High (~1.10%)	Fine (~1.37)	Medium (~7.4)	High (~74%)	Medium–low (~13%)	Medium (~0.43)	87	60	5	0

SCM chemical composition values show that the $\text{SiO}_2+\text{Al}_2\text{O}_3$ ratios remain constant at high levels (~68–75%) across all MCCI ranges, while the CaO ratio exhibits a significant decreasing trend as MCCI increases. While the CaO content is approximately 26% in the low MCCI range, it decreases to 20% in the medium range, 18% in the high range, and 13% in the very high range. This suggests that as the compatibility level increases, the chemical composition of the systems transforms to a structure with lower CaO content but richer in pozzolanic oxides ($\text{SiO}_2+\text{Al}_2\text{O}_3$). However, the ~13% CaO content observed in the high MCCI ranges is not low in absolute terms, but rather corresponds to a moderate CaO composition. This value is above the level provided by typical natural pozzolans (mostly 1–5% CaO), indicating that such compositions can be achieved by combinations of SCMs with different properties rather than by a single SCM. Consequently, high MCCI values are characterized by low to moderate CaO and high $\text{SiO}_2+\text{Al}_2\text{O}_3$ contents.

The water/binder (w/b) ratio is observed to be high at an average value of ~0.48 in the low MCCI range, decreasing to ~0.45 in the medium range, ~0.44 in the high range, and ~0.43 in the very high range. This gradual decrease indicates that systems with high MCCI values can operate with lower water requirements. This trend is directly related to increasing superplasticizer (SP): while SP content remains at 0.37–0.47% in the low and medium MCCI ranges, they rise to 0.70% in the high range and 1.10% in the very high range. Therefore, thanks to the increased SP, lower water/binder ratios are possible while maintaining workability; this allows the hydration products to form a denser matrix, improve pore structure, and support strength development. The literature also indicates that low w/b ratios reduce porosity, allow hydration products to develop more compactly, and have positive effects on both strength and durability. In this context, the inverse relationship between MCCI and w/b ratio can be considered one of the important indicators of system compatibility.

The distribution of SP types reveals significant differences in PCE, PMS, PNS, and LHA contents across different MCCI ranges. PMS and PNS additives are particularly prominent in the medium (0.30–0.45) and high (0.45–0.60) MCCI ranges, supporting the PC-SCM-SP compatibility. PCA additives become more prevalent in the high and very high MCCI ranges, becoming a determining factor at high compatibility levels. LHA additives persist in the low, medium, and moderately high ranges, but disappear completely in the very high MCCI range. In short, each additive type is prominent at

different MCCI levels, with PMS and PNS playing a dominant role in the medium-high range, PCE in the high and very high ranges, and LHA in the low and medium ranges. This distribution demonstrates that SP types of shape system compatibility to different degrees, with each additive becoming prominent in specific MCCI ranges, depending on its specific function. PCE is becoming more common in the high and very high MCCI ranges and stands out as a decisive SP type in compatibility thanks to its superior dispersion capacity and ability to maintain workability even at low water/binder ratios.

When all the parameters in Table 5.15 are evaluated, low MCCI ranges are defined by high OPC contents and low SP content; it is noteworthy that as MCCI increases, the OPC ratio decreases, the SP content increase significantly and the w/b ratio decreases gradually. This trend leads to the prominence of mixtures that can operate with lower water requirements and maintain their workability thanks to highly efficient superplasticizers. At the same time, maintaining high levels of $\text{SiO}_2+\text{Al}_2\text{O}_3$ ratios with the decrease in CaO content indicates that SCMs play a more effective role and that the hydration process progresses in a more balanced manner. The fact that SCM particle size parameters remain constant across all ranges reveals that compatibility is essentially more strongly related to chemical composition and rheological parameters. The differences in the distribution of SP types also show that each additive shapes compatibility through different mechanisms and that this diversity directs system performance. In conclusion, systems achieving high MCCI values are characterized by low OPC–high SCM content, increased PCE contribution, low w/b ratio and chemical content rich in $\text{SiO}_2+\text{Al}_2\text{O}_3$, and these findings clearly reveal the main determinants of multi-criteria compatibility. Furthermore, the fact that the CaO content is not at very low levels indicates that such compositions can often be obtained by using SCMs with different properties (e.g., binary or ternary combinations) instead of a single SCM.

As a result, the Multi-Criteria Compatibility Index (MCCI) stands out as a holistic assessment tool that goes beyond the one-dimensional evaluation approaches in literature. The common approach in literature generally bases compatibility assessment on single parameters (e.g., flowability, hydration kinetics, compressive strength), making it difficult to achieve a holistic and comparable assessment across different binder systems. On the other hand, MCCI combines multiple parameters into a single score by normalizing and weighting them, thus providing a flexible and adaptable framework where different criteria are considered simultaneously. One of the most important features

of MCCI is its adaptability to different binder systems and operating conditions. The type and weighting of the criteria used in calculating MCCI can be adjusted according to the requirements of the system being studied. For example, in this thesis, hydration kinetics, CH content, and compressive strength are considered together; however, the index's flexible nature allows for the inclusion of additional criteria in different applications. In a previous study, rheological parameters were also included in MCCI [168]. In this respect, the MCCI can serve as a practical decision-making tool not only for evaluating existing data but also for preliminary screening of new mix designs.

The MCCI also offers a standardized and comparative assessment. The ability to compare different PC-SCM-SP combinations with a single score provides significant convenience for both academic research and industrial applications. Thus, the design of blended cements that comply with low-carbon targets and meet performance expectations can be based not only on experimental observations but also on numerical and holistic evaluation output. This offers a critical contribution, particularly in material selection, given the diversity and supply constraints of SCM candidates. In conclusion, the MCCI can be considered both a research tool that addresses gaps in the literature and a design tool adaptable to different conditions in practice. Such a methodological framework not only enables a more accurate interpretation of the multidimensional interactions in PC-SCM-SP systems but also provides a strong foundation for the widespread adoption of low-carbon blended Portland cements.

Chapter 6

Conclusions and Future Prospects

6.1 Conclusions

This thesis comprehensively investigates the multidimensional interactions between Portland cement (PC), supplementary cementitious materials (SCM), and superplasticizers (SP) for the development of low-carbon, high-performance blended Portland cements. The cement sector, responsible for 6–8% of worldwide CO₂ emissions, must adopt low-carbon manufacturing as a need rather than a simple environmental choice.. In this context, the primary objective of this study is to assess the compatibility of components using both individual performance metrics and a comprehensive approach that includes hydration kinetics, pozzolanic activity, and compressive strength parameters, to inform the design of blended cements intended to decrease Portland cement usage.. To this end, a comprehensive experimental dataset was generated, and these data were analyzed using regression-based machine learning models to yield highly accurate predictions. Finally, by normalizing and weighting the different criteria, the Multi-Criteria Compatibility Index (MCCI) was developed and applied to a comprehensive dataset to reveal the key parameters of compatibility in PC–SCM–SP systems. The following conclusions can be drawn based on the experimental and computational results of this study.

1. Hydration kinetics in superplasticized blended cements are mainly controlled by SCM replacement level, oxide composition, and SP content. Fine, high-SiO₂+Al₂O₃ SCMs (NP, CC) accelerate early hydration through nucleation and pozzolanic reactions, while CaO-rich BFS enhances both early and late hydration via latent hydraulic activity. CC shows dual behavior—initial acceleration followed by short-term slowdown and strong late heat evolution. Low w/b ratios intensify early peaks. Among SPs, PNS sustains early reactivity, whereas LHA

delays early hydration but enhances long-term heat. Hydration behavior depends on the synergy between SCM chemistry, fineness, and SP–w/b design.

2. CH content is primarily influenced by SCM chemistry, replacement level, and SP–w/b interaction. High-SiO₂+Al₂O₃ SCMs (NP, CC) rapidly consume CH and promote secondary C–S–H formation, whereas CaO-rich BFS reacts gradually through latent hydraulic activity. Increasing SCM content reduces CH at both 3 and 28 days, while higher w/b ratios slightly increase it but remain below control due to pozzolanic action. SPs can accelerate hydration, but their effect is minor compared to SCM reactivity. Optimizing SCM type and replacement with appropriate SP–w/b balance enhances CH consumption, densification, and durability.
3. Compressive strength is mainly governed by SP content, SCM fineness, and chemistry. Fine SCMs and low w/b ratios enhance early strength via matrix densification, while high-SiO₂+Al₂O₃ SCMs (NP, CC) increase long-term strength through pozzolanic reactions. BFS contributes to both early and late strength due to latent hydraulic activity. Among SPs, PCE improves early strength via dispersion, whereas LHA may reduce or enhance strength depending on its compatibility. Simultaneous optimization of SP dosage, SCM fineness, and chemical composition is essential to achieve balanced early performance and long-term durability.
4. Machine learning effectively modeled the complex multivariate relationships in superplasticized blended cements. Early-age strength, driven by physical parameters, was well captured by linear regression, whereas nonlinear models better predicted hydration kinetics, CH content, and long-term strength. GPR and NN achieved the highest accuracy ($R^2 \approx 0.90\text{--}0.97$). GPR performed more consistently for stable outputs, while NNs excelled in complex, high-variance data. These results highlight ML's ability to capture hidden interactions among SCM type, level, and SP content, enabling faster and more accurate performance prediction for sustainable cement design.
5. Hyperparameter tuning improved model performance, especially for GPR, by reducing error and enhancing R^2 . Random Search was preferred for efficiency over large parameter spaces. However, improvements were limited for complex models like neural networks, where overfitting risk increased with small datasets or high-variance outputs. This indicates that tuning must be carefully balanced—

beneficial for simple, stable models but potentially detrimental for highly nonlinear ones. Effective optimization depends on model complexity and data characteristics, aiming to improve generalization rather than only training accuracy.

6. F-test results confirmed that SCM properties dominate model predictability. For hydration kinetics, SCM chemistry and particle size were the main drivers, while SP content and w/b played secondary roles. CH content was most influenced by SP dosage and SCM composition, whereas compressive strength was governed by w/b ratio, OPC content, and SCM fineness. The consistent dominance of physical and chemical attributes supports the packing–reactivity paradigm, emphasizing w/b ratio, SCM fineness/chemistry, and SP dosage as key determinants of performance and model accuracy.
7. The Multi-Criteria Compatibility Index (MCCI), developed in this thesis, provides a holistic framework that surpasses traditional single-parameter approaches for evaluating the compatibility of PC–SCM–SP systems. By normalizing and weighting multiple performance indicators, MCCI integrates hydration kinetics, CH content, and compressive strength into a single metric. Analysis of 1602 synthetically generated mixtures showed that higher MCCI values correspond to lower OPC and higher SCM contents, supported by increased SP dosages and low w/b ratios. High-compatibility mixtures typically contained SCMs with low-to-moderate CaO and high $\text{SiO}_2 + \text{Al}_2\text{O}_3$ levels, while SP distribution shifted from PNS/PMS to PCE with increasing compatibility. Overall, MCCI serves as a robust and adaptable tool for both evaluating existing systems and guiding the design of low-carbon, high-performance blended cements.

6.2 Societal Impact and Contribution to Global Sustainability

This thesis presents an approach that aims to reduce the environmental burden by reducing the amount of Portland cement while simultaneously maintaining high performance targets. The developed multi-criteria compatibility index (MCCI) and machine learning modeling methods provide the ability to holistically evaluate the

complex interactions of different components (PC-SCM-SP), filling a significant gap in both academic and industrial perspectives. Thus, high SCM substitution reduces the amount of Portland cement, while enabling the design of next-generation binder systems without compromising early- and late-age performance targets. This will make tangible contributions to reducing the cement industry's carbon footprint.

The machine learning methods used in the study accelerate experimental processes, reducing resource and energy consumption, thus supporting sustainable production approaches. The developed models can make highly accurate predictions even under complex parameter sets, significantly shortening the traditionally time-consuming laboratory and trial-and-error design processes. This approach will facilitate the widespread adoption of low-cost, fast, and data-driven decision-making processes. Furthermore, MCCI's adaptability to different cementitious systems enables the development of low-carbon, high-performance designs tailored to local and regional conditions. This also provides indirect societal benefits, such as reducing supply chain constraints, more efficient use of local resources, and supporting economic circularity. Ultimately, this study contributes to the development of a cement sector that is not only environmentally but also socio-economically sustainable.

6.3 Future Prospects

The machine learning modeling approach developed in this study and the MCCI offer an innovative framework that can holistically evaluate the complex interactions of components in cementitious systems. The findings demonstrate that mixtures containing high amounts of SCM, when used in conjunction with appropriate superplasticizers and low w/b ratios, can achieve high performance both in the early and long term. These results hold significant potential for the widespread adoption of low-carbon binder systems in the future.

Future studies are expected to incorporate more parameters (e.g., durability, rheology, environmental impact indicators, etc.) by leveraging the flexible nature of the MCCI. This will enable holistic evaluation of not only mechanical performance but also durability and environmental sustainability indicators. Furthermore, integrating literature and/or cement industry data into the model training process in future studies will increase the reliability of the predictions. Larger datasets will strengthen the generalizability of the

models and increase the adaptability of the MCCI to different cementitious systems. In conclusion, the methodological framework presented in this study is expected to be one of the fundamental tools to guide the development of data-driven, low-carbon and high-performance blended cement systems in both academic and industrial applications in the future.



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APPENDIX

Table A.1 — Minimum, maximum, and mean values of input variables for the training dataset (80%)

Dataset	Input Variable	Min	Max	Mean
Isothermal Calorimetry	OPC (%)	40	100	66.9
	SP (%)	0.03	2.0	0.59
	SCM d ₅₀ (μm)	4.0	20.0	8.5
	Water/binder ratio	0.35	0.55	0.45
	SCM SiO ₂ + Al ₂ O ₃ (%)	49.5	90.8	72.0
	SCM CaO (%)	0.2	37.7	10.5
Thermal Analysis (TGA)	OPC (%)	45	80	68.9
	SP (%)	0.03	1.7	0.55
	SCM d ₅₀ (μm)	4	20	9.6
	Water/binder ratio	0.4	0.55	0.47
	SCM SiO ₂ + Al ₂ O ₃ (%)	48.8	90.8	74.7
	SCM CaO content (%)	0.2	37.7	10.4
Compressive Strength	OPC (%)	45	100	71.2
	SP (%)	0	1.54	0.54
	SCM d ₁₀ (μm)	0.70	1.90	1.32
	Water/binder ratio	0.40	0.50	0.44
	SCM SiO ₂ + Al ₂ O ₃ (%)	48.8	90.8	69.1

Table A.2 — Minimum, maximum, and mean values of input variables for the testing dataset (20%)

Dataset	Input Variable	Min	Max	Mean
Isothermal Calorimetry	OPC (%)	40	100	66.7
	SP (%)	0.03	1.5	0.63
	SCM d ₅₀ (μm)	4.0	20.0	7.1
	Water/binder ratio	0.35	0.55	0.47
	SCM SiO ₂ + Al ₂ O ₃ (%)	49.5	90.8	70.6
	SCM CaO (%)	0.2	37.7	8.7

Thermal Analysis (TGA)	OPC (%)	45	80	72
	SP (%)	0.07	1.6	0.58
	SCM d ₅₀ (μm)	4.0	20.0	10.1
	Water/binder ratio	0.40	0.55	0.47
	SCM SiO ₂ + Al ₂ O ₃ (%)	48.8	90.8	73.5
	SCM CaO content (%)	0.2	37.7	10.4
Compressive Strength	OPC (%)	45	100	73.4
	SP (%)	0	1.54	0.5
	SCM d ₁₀ (μm)	0.7	1.9	1.3
	Water/binder ratio	0.40	0.50	0.44
	SCM SiO ₂ + Al ₂ O ₃ (%)	48.8	90.8	67.7

Table A.3 — Minimum, maximum, and mean values of output variables for the training dataset (80%)

Dataset	Output Variable	Min	Max	Mean
Isothermal Calorimetry	Onset time (min)	60	1542	185.4
	Onset heat (mW/g cement)	0.25	2.3	0.87
	Induction period (min)	45	1100	192.3
	Total heat at 72 h (J/g cement)	112	451	347.3
Thermal Analysis (TGA)	Relative CH content at 3 days (%)	27.6	114.5	81.3
	Relative CH content at 28 days (%)	0	86.6	52.1
Compressive Strength	@ 2 days (MPa)	4.2	28.0	13.9
	@ 7 days (MPa)	9.3	42.6	23.4
	@ 28 days (MPa)	15.9	52.7	32.5
	@ 90 days (MPa)	17.1	54.3	35.8

Table A.4 — Minimum, maximum, and mean values of output variables for the testing dataset (20%)

Dataset	Output Variable	Min	Max	Mean
Isothermal Calorimetry	Onset time (min)	62	760	176.8
	Onset heat (mW/g cement)	0.3	2.3	0.87
	Induction period (min)	45	1100	190.4
	Total heat at 72 h (J/g cement)	262	451	353.0
Thermal Analysis (TGA)	Relative CH content at 3 days (%)	35.5	114.5	84.9
	Relative CH content at 28 days (%)	0	85.5	57.0
Compressive Strength	@ 2 days (MPa)	6.0	28.0	13.8
	@ 7 days (MPa)	13.3	36.8	22.7
	@ 28 days (MPa)	22.6	41.2	30.5
	@ 90 days (MPa)	18.1	54.3	37.8

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