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Marine Pie

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Low Carbon Concrete: Alkali-activation of waste calcined clay

University of Dundee



Notice analytique

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Titre (français)	Béton bas-carbone: Activation alcaline de déchets d'argile calcinée.		
Titre (anglais)	Low Carbon Concrete: Alkali-activation of waste calcined clay.		
Résumé (français)	<p>Le projet explore une méthode appropriée pour l'activation alcaline d'une gamme d'argiles calcinées de couches de recouvrement et d'interstrates afin de développer un béton à faible teneur en carbone.</p> <p>Le projet se concentrera ensuite sur le processus de calcination d'une argile réutilisée afin de concilier performance et faible consommation d'énergie.</p>		
Résumé (anglais)	<p>The project explores a suitable method for alkali-activating a range of overburden and interburden calcined clays to develop low carbon concrete. The project will then focus on the calcination process of a waste clay in order to balance performance and low-energy consumption.</p>		
Mots-clés (français, 5 maxi)	Béton bas-carbone, matériaux alcalin-activés, argile calcinée, processus de calcination, consommation d'énergie.		
Mots-clés (anglais, 5 maxi)	Low-carbon concrete, alkali-activated materials, calcined clay, calcination process, energy consumption.		
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	68	5	22

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Le travail présenté distingue explicitement ce que j'ai produit de ce que j'ai emprunté à d'autres. A ce titre, les citations sont clairement identifiables et les sources (écrits, images) qui ont alimenté ma réflexion sont référencées.

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More than a professional experience, this internship was a real life experience for me.

Abstract

This study investigates the potential of waste clay for producing alkali-activated calcined clay as a sustainable substitute for ordinary Portland cement in the construction industry. Using a range of analytical techniques, two calcined clays and one raw clay were collected and characterized to identify the optimal alkali-activating solution. The chemical and mineralogical compositions of the clays were key in determining the most effective activation strategies.

The research is divided into two main parts:

- The first part evaluates the performances of the two calcined clays using experiments such as setting time, compressive strength and carbonation tests;
- The second part focuses on optimising the calcination process, identifying the best temperature and duration to maximize performance while minimising energy consumption.

Key findings include:

- Chemical and mineralogical compositions are crucial for tailoring activation solutions to each clay type due to significant variability in results. Indeed, both Si/Al and SiO₂/Na₂O ratios are decisive in this process.
- Iron content significantly impacts clay reactivity and performance, warranting further investigation to better define its role.
- Calcination at 750°C for 40 minutes was found to optimise both reactivity and material performance. To avoid incomplete phase transformation, calcination should be conducted on a tray or in a rotary kiln, potentially reducing energy consumption.

The study concludes that alkali-activated calcined clays show promise as a viable alternative to traditional cement, with the low-iron content clay demonstrating excellent performance, being easy to activate and practical for use.

Abbreviations

GHG	greenhouse gas
EU	European Union
EN	European Norm
PC	Portland cement
FA	fly ash
GGBS	ground granulated blast furnace slag
LS	limestone
CC	calcined clay
w/c ratio	water to cement ratio
SSA	specific surface area

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1. Introduction

1.1 Background

In 2015, 196 parties at the 21st UN Climate Change Conference (COP21) adopted the Paris Agreement. Its main goal is to keep “the increase in the global average temperature to well below 2°C above pre-industrial levels” and to continue efforts “to limit the temperature increase to 1.5°C above pre-industrial levels”.¹ However, reaching this limit is getting closer than we might think. According to Copernicus, the European Union's Earth observation programme, global warming reached an estimated 1.28°C in June 2024.²

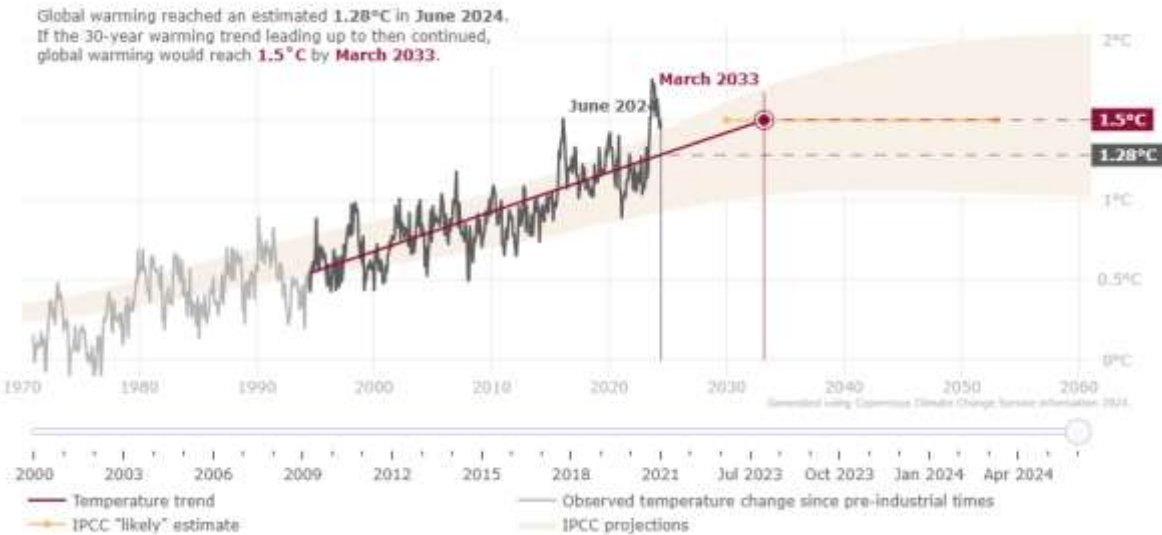


Figure 1.1 Global warming evolution since 1970
(C3S, 2024)

The Intergovernmental Panel on Climate Change (IPCC), which is the UN's organisation responsible for evaluating climate science, regularly reviews and summarises the scientific evidence of climate change, its impacts, future risks, and strategies for adaptation and mitigation. They particularly observed that human activities are the main cause of global warming, through the emission of GHG. This has led to significant and rapid changes across

¹ The Paris Agreement | UNFCCC, United Nations Climate Change

² Global temperature trend monitor (copernicus.eu)

the Earth's systems, affecting many weathers and climates in all regions worldwide. Unfortunately, communities that are most vulnerable and least responsible for climate change are disproportionately affected. (IPCC, 2023).

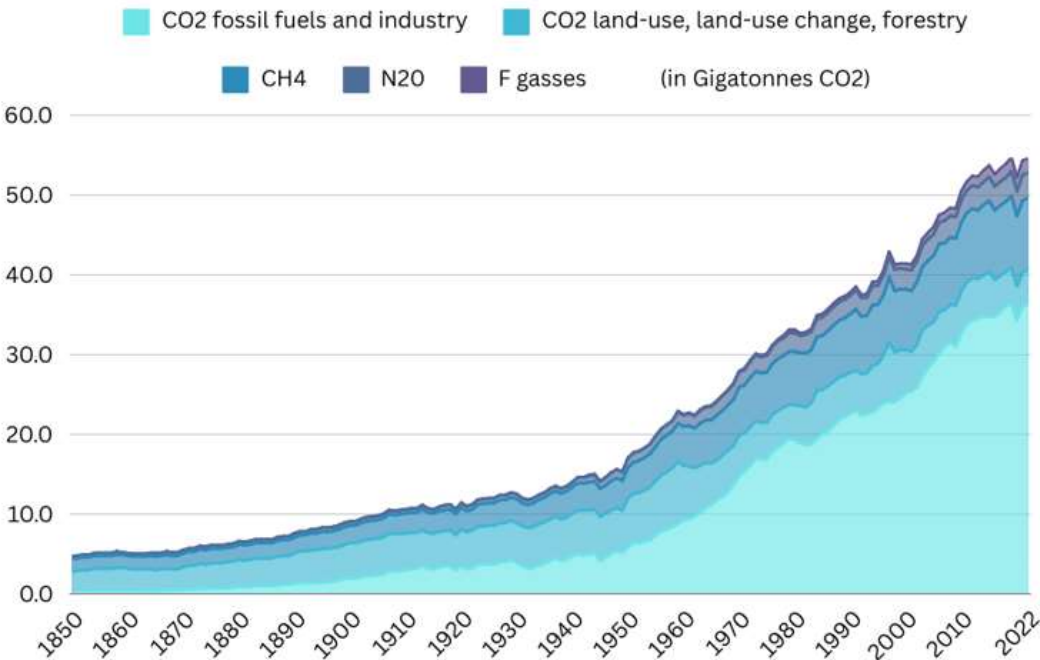


Figure 1.2 Evolution of GHG emissions since 1850
(Calvin et al., 2023)

Facing this observation, climate emergency has been a major issue for years. The European Union has made fighting climate change an explicit objective of its environmental policy. Various laws and promotions have been implemented to achieve this goal: the European Green Deal (2019) commits the EU to reach carbon neutrality by 2050, while the European Climate Law (2021) legally ensures this climate-neutral target. Additionally, the EU encourages the development of green transport, energy efficiency renovation of buildings, and expansion of renewable energy, among other efforts.

At the same time, it is generally accepted that the cement industry represents about 7% of CO₂ global emissions, and about 4% within the European Union. (IEA, 2018). However, the global demand for concrete remains significant, whether in developed or developing countries, where it is increasing promptly. In response to this reality, various researches have been conducted to find alternatives to PC, which is a major contributor to GHG emissions.

1.2 Overall aim and objectives

This research aims to explore the potential of alkali-activation of waste clay for producing industrial concrete. The process is intended to be simple, scalable and relevant to the industry. Indeed, the main objective is to decrease the GHG emissions associated with industrial concrete production.

The specific objectives of this research are:

- Characterise various types of clay using techniques such as X-ray Diffraction (XRD) and X-ray Fluorescence (XRF);
- Develop suitable alkali-activation methodologies for each type of calcined clay;
- Optimise the mix design for calcined clays to achieve adequate activation, using a range of parameters defined in previous studies on the alkali-activation of geopolymers;
- Obtain setting times between 3 and 8 hours;
- Optimise the calcination process of raw clay to determine the most energy-efficient protocol.

1.3 Research scope

This research involved the characterisation of two different calcined clays to determine suitable alkali-activation processes. Initially, each clay was activated using three different solutions, based on previous research studies. These solutions were then adjusted until the activation time was considered optimal. The optimisation parameters included alkaline ratio ($\text{SiO}_2/\text{Na}_2\text{O}$ in the alkaline solution), the Si/Al ratio of the mix, and the w/c ratio. A series of tests were then carried out to evaluate the reactivity of each calcined clay and the strength of the resulting paste.

Meanwhile, nine samples of a raw clay were calcined following a flash process at 650°C, 750°C and 850°C for durations of 20, 40 and 60 minutes. Few experiments were then performed to determine the most effective process based on the reactivity of the calcined clay.

1.4 Layout of the report

This report includes six chapters as described below:

- Chapter 1 provides a brief overview of the research background, aims, objectives, and scope. The structure of the report is also introduced.
- Chapter 2 explores European policies related to low-carbon concrete, focusing on roadmaps and Eurocodes, with particular attention to the use of clay in France and the energy consumption of its calcination.
- Chapter 3 details the research approach, including the methodology for clay characterisation and a description of the experimental procedures.
- Chapter 4 presents an analysis and discussion of the results obtained from the experiments.
- Chapter 5 concludes the report by summarising the findings from all chapters and offering recommendations for future research.

2. Litterature review

2.1 Roadmaps for Net Zero Concrete

In keeping with the Paris Agreement's objective to limit global warming to well below 2°C, various cement and concrete associations worldwide have developed aimroadmaps aimed at achieving Net Zero Concrete by 2050. These roadmaps, while customised to the specific needs of each region or country, share a common goal: to drastically reduce the carbon footprint of cement production, a critical component of global CO₂ emissions.

These associations vary in scope and influence. On a global scale, the Global Cement and Concrete Association (GCCA) represents approximately 80% of the world's cement industry outside of China, driving international efforts towards sustainable cement production. On a national level, organisations like the Mineral Products Association (MPA) focus on specific markets, such as the United Kingdom, where they represent the major Portland cement manufacturers.

Despite differences in regional targets and timelines, particularly for 2030 goals, the strategies proposed by these associations converge on several key approaches:

- Carbon Capture, Use, and Storage (CCUS): A key technology to reduce emissions by capturing CO₂ during cement production which is then stored underground and/or used in other processes;
- Reduction in Clinker Production: As clinker is responsible for up to 98% of the carbon footprint in cement, a strong focus is placed on reducing its usage through more efficient production processes and alternative materials.
- Low Carbon Cements and Recycled Materials: The industry is increasingly focusing on developing cements that use recycled materials and alternative binders to replace traditional clinker.

The focus on clinker reduction is especially critical. Clinker, the key ingredient in traditional PC, is not only energy-intensive to produce but also emits large quantities of CO₂ during its manufacturing process. Therefore, exploring alternatives to it, such as low carbon cements, is essential to reduce the overall carbon footprint of cement.

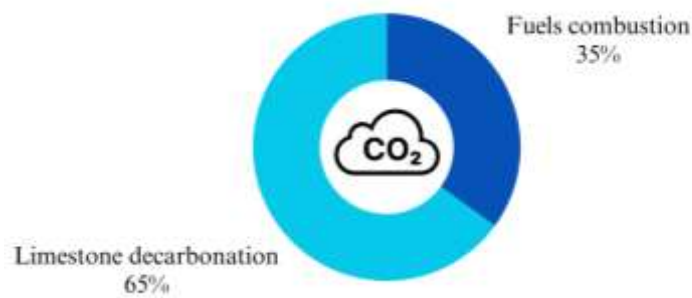


Figure 2.1 CO₂ emissions repartition in the clinker
(IEA, 2018)

The following table summarises the key goals and strategies outlined by various cement and concrete associations worldwide. Each roadmap reflects the association's commitment to achieving significant carbon reductions by 2030 and reaching net zero emissions by 2050, following global climate objectives.

Table 2.1 Associations' roadmaps keypoints

Association	Geographical Scope	Publication date	2050 Goals	2030 Goals	Strategies
CEMBUREAU	Europe	2020	Carbon neutrality	<ul style="list-style-type: none"> -30% CO₂ for cement -40% CO₂ for value chain 	<ul style="list-style-type: none"> Carbon Capture, Use and Storage (CCUS); Biomass waste; Low carbon-cements; Optimized concrete mixes.
GCCA	Global	2020	Net Zero Carbon Emissions	<ul style="list-style-type: none"> -25% CO₂ 	<ul style="list-style-type: none"> Carbon Capture, Use and Storage (CCUS); Savings in clinker production; Savings in cement and binders.
IEA	Global	2018	24 % CO ₂ reduction below current levels	<ul style="list-style-type: none"> Significant energy efficiency; Alternative fuels; Clinker substitution. 	<ul style="list-style-type: none"> Carbon Capture, Use and Storage (CCUS); Supportive policies; Public-private collaboration.
LCCG (ICE and GCB)	Global	2022	Low Carbon Concrete	<ul style="list-style-type: none"> Decarbonizing concrete production; Efficient use of concrete. 	<ul style="list-style-type: none"> Carbon Capture, Use and Storage (CCUS); Clinker reduction; Long lived storage for any greenhouse gases (GHG) produced.
MPA	UK	2020	Net Zero Carbon Emissions	<ul style="list-style-type: none"> -50% CO₂ emissions compared to 1990. 	<ul style="list-style-type: none"> Carbon capture, usage and storage (CCUS); Energy efficiency; Use of recycled materials; Thermal mass.
PCA	USA	2021	Carbon Neutrality	<ul style="list-style-type: none"> -30% CO₂ per ton of cementitious product. 	<ul style="list-style-type: none"> Alternative fuels; Clinker substitution; Energy efficiency.
VDZ	Germany	2019	Carbon Neutrality	<ul style="list-style-type: none"> -30% CO₂ compared to 1990; 60% alternative fuels usage. 	<ul style="list-style-type: none"> Alternative fuels; Clinker reduction; Energy efficiency.

While each roadmap aims for carbon neutrality by 2050, the diverse intermediate goals for 2030 reflect different regional priorities and capabilities. For instance, global associations like GCCA have to adjust to a wide range of production conditions and policies, leading to a more flexible approach. In contrast, associations like MPA and PCA, which focus on national contexts, can adapt their strategies more precisely to local policies and market conditions.

Nevertheless, the strategies underlined are not easily deployable. For example, only 20% of cement's plants in France would meet the criteria for CCUS expansion, only because of their location. (ADEME, 2020). Moreover, the investment required is estimated at 200 million euros per site (for an average annual production of 600 kt of cement). Taking into account the restrictions due in particular to the operating and landfill costs of this capture (South-East and North of France), the capture potential is limited to 2.5 MtCO₂ for the cement plants in the region. In its roadmap, the SFIC has identified a potential for the capture and storage of 5 MtCO₂e by CCUS technologies, which would make it possible to achieve the industry's 80% emissions reduction target. (SFIC and CNI, 2021). Nevertheless, using CCUS would induced an additional cost on cement, in the current economic context, of at least 80 €/t to 100 €/t, which can be dissuasive in the context of traditional free competition. (The Shift Project, 2022).

Hence, although solutions to decrease GHG emissions of the construction industry are known, the successful implementation of these roadmaps will require not only technological advancements but also significant investments and supportive policy frameworks.

2.2 Standards and policies

2.2.1 Overview

Standards and policies are foundational to the cement and concrete industry, shaping everything from production methods to environmental impact. They ensure that the materials used in construction meet minimum safety and performance criteria, which is essential for the structural integrity of buildings and infrastructure. This is particularly important in an industry where the long-term durability of materials can have significant implications for public safety and economic costs.

Furthermore, policies at both national and European levels guide the industry towards achieving environmental and economic goals. These include reducing carbon emissions, enhancing energy efficiency, and promoting the use of recycled materials. For instance, the European

Union's Green Deal provides a regulatory framework for a low-carbon economy, while the *Réglementation Environnementale* (RE2020) set ambitious targets to reduce the environmental footprint of buildings in France, pushing the industry to innovate and adopt more sustainable practices.

Beyond environmental considerations, standards and policies also facilitate international trade by ensuring compatibility within the EU. Indeed, the EN system allows the free circulation of products, by removing trade barriers, and facilitates the implementation of new products in every country, contributing to economic stability and growth.

Besides, a French adaptation has been undertaken through the NF EN system, to ensure that standards are directly applicable in the French context, considering local materials, practices, and environmental objectives. Additionally, French regulations often include stricter requirements in areas such as energy efficiency and environmental impact, driven by national policies like the RE2020.

2.2.2 EN 197-1

This standard classifies cements into several categories based on their composition, particularly the proportion of clinker. (*Appendix 1*). It sets the requirements for their chemical composition and performance characteristics, ensuring that they meet necessary safety and durability standards. The use of the following SCMs are allowed: FA, GGBS, silica fume, natural pozzolans, burnt slate and LS. The following table summarizes the contents of some of the European cements, as given in EN 197-1. (Sri Ravindrarajah, 2010).

Table 2.2 Portland Composite cements according to EN 197-1

Cement Type	Clinker (%)	Slag (%)	SCM (%)	Limestone (%)
Portland Limestone Cement				
CEM II/A-L	80 - 94	-	-	6 - 20
CEM II/B-L	65 - 79	-	-	21 - 35
Portland Composite Cement	Combination of slag, silica fume, fly ash, pozzolans, burnt shale and limestone			
CEM II/A-M	80 - 94	6 - 20		
CEM II/B-M	65 - 79	21 - 35		
Blast-Furnace Cement				
CEM III/A	35 - 64	36 - 65	-	-
CEM III/B	20 - 34	66 - 80	-	-
CEM III/C	5 - 19	81 - 95	-	-
Pozzolan Cement	Combination of silica fume, fly ash and pozzolan			
CEM IV/A	65 - 89	-	11 - 35	-
CEM IV/B	45 - 64	-	36 - 55	-
Composite Cement	Combination of slag, low-calcium fly ash and pozzolan			
CEM V/A	40 - 64	18 - 30	18 - 30	-
CEM V/B	20 - 38	31 - 50	31 - 50	-

While this standard explicitly outlines performance criteria, it is regrettable that environmental considerations are not addressed, despite their importance in the selection of cement types. The following graph illustrates the carbon footprint of each cement type, providing a visual representation of how these classifications impact the overall environmental performance of cement products.

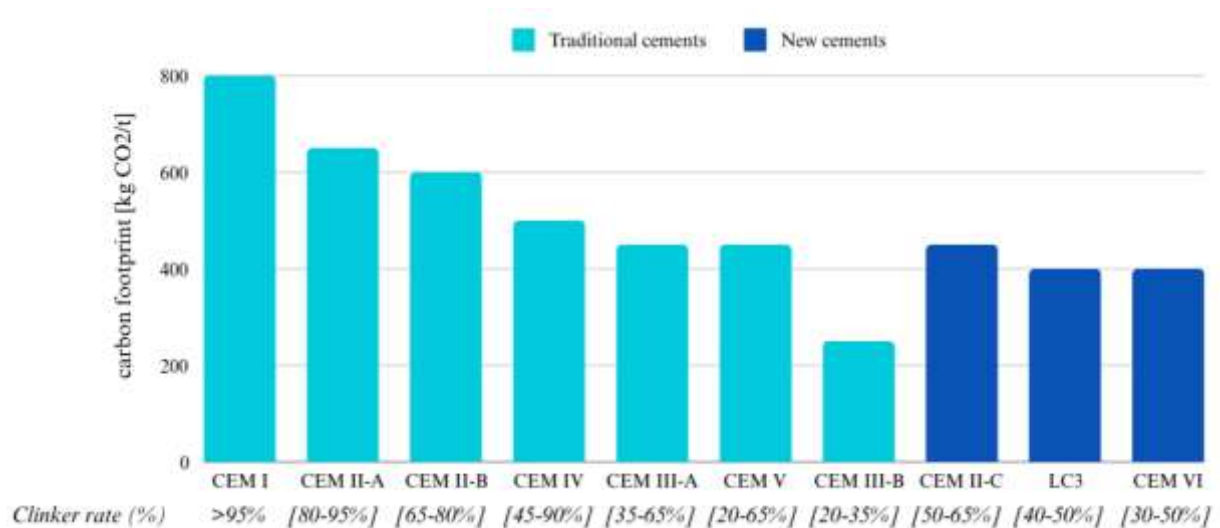


Figure 2.2 Carbon intensity by cement type.³

(The Shift Project, 2022)

Naturally, the carbon footprint is a function of the clinker rate: the graph clearly illustrates how reducing clinker content directly lowers CO₂ emissions. That is why replacing 50% of clinker is one of the main objectives to develop a low-carbon concrete.

However, it's essential to note that while the reduction in clinker content is a powerful tool for lowering carbon emissions, it must be balanced with maintaining the mechanical properties and durability of the concrete. Alternative materials play a crucial role in this, as they not only reduce the carbon footprint but also contribute to the long-term performance of the concrete in specific applications. For example, it is shown that a 20% replacement of cement by calcined clay can increase the compressive strength by 12% compared to the reference mortar. (Boakye and Khorami, 2021).

The standardisation of lower-carbon cements demonstrates a shift in the industry toward more sustainable practices. Yet, challenges remain in ensuring that these materials are as widely adopted and understood as traditional cements like PC. For example, there might be variations in the availability of SCMs, regional differences in construction practices, or even trust issues with these less familiar materials. That is some reason why the new standardised cements in EN 197-5 have not been fully adopted in the construction industry, not to mention the long time took to include these new cements in the norm. Around 5 to 7 years were needed to legally introduce these cements in this standard in 2021, and even more time is needed to adapt the EN

³ The new cements are cements included in the EN 197-5

206 regarding the concrete. While reducing the impact of concrete is an emergency, it is regrettable that governments take so much time to do these changes.

2.2.3 EN 206

EN 206 is the European standard that governs the specification, performance, production, and conformity of concrete. It provides the essential guidelines that ensure concrete used across various construction projects meets the necessary quality and safety criteria. This standard is widely adopted across Europe and is a major document for anyone involved in the construction industry.

The standard defines classes of concrete properties in order to be applied in a wide range of climates, geographical conditions, regional traditions and experiences, with different levels of protection. It is designed to work with several other standards, especially EN 197-1. The relationship between EN 206 and the cement standards it references is crucial. Indeed, the performance of concrete is directly influenced by the characteristics of the cement used, which is why updates to cement standards, such as the introduction of low carbon cements in EN 197-5, necessitate careful consideration and eventual adaptation of EN 206. (ILNAS, 2022).

Besides, the relationship between EN 206-1 and other standards are illustrated in the following figure.

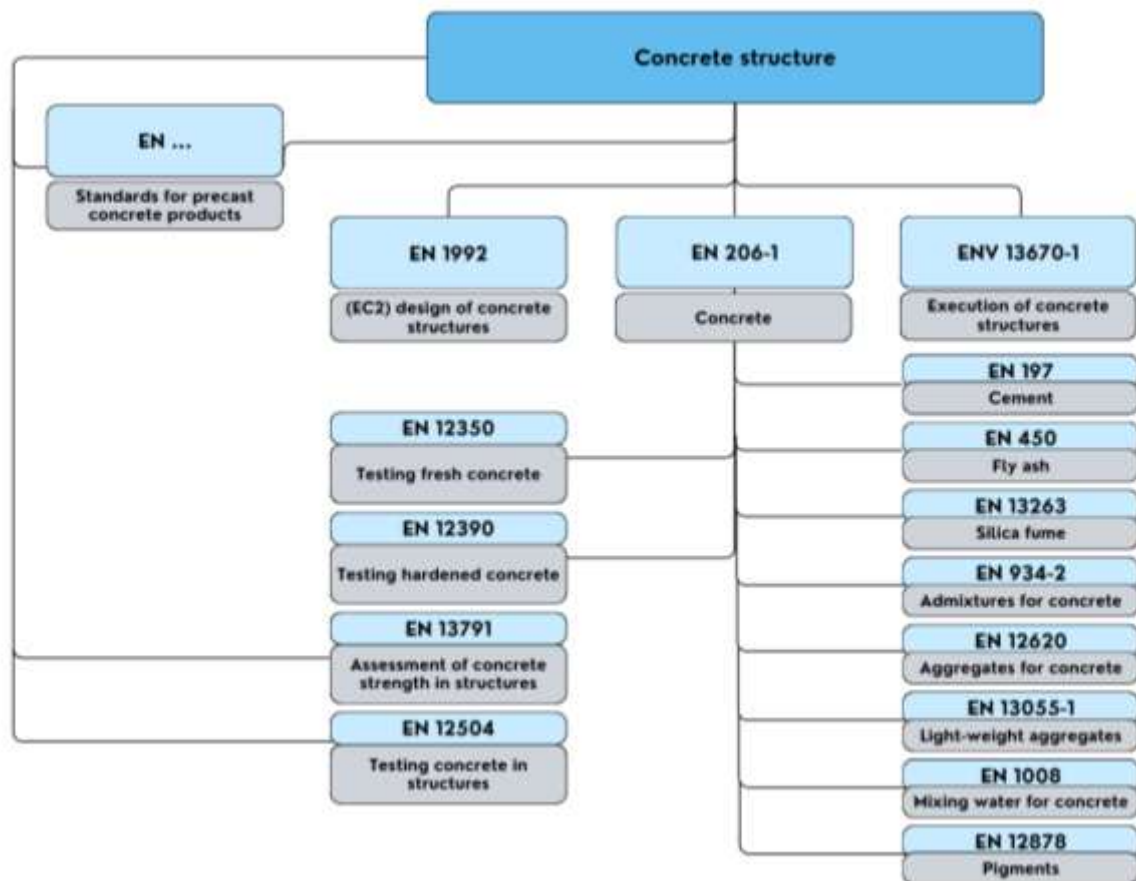


Figure 2.3 Relationship between En 206-1 and other standards

(Müller, 2012)

Collectively, these standards ensure that concrete is properly specified, tested, and executed to meet safety, performance, and durability requirements. However, while standardisation is crucial for ensuring quality and consistency, it also presents several challenges:

- Increased costs: due to compliance, testing, and implementation expenses;
- Administrative complexity: due to extensive documentation and administrative burden;
- Innovation slowdown: due to the meticulous validation processes and the focus on established materials rather than lower-carbon alternatives;
- Sustainability absence: due to the lack of environmental considerations.

These challenges highlight the need for a balanced approach to standardisation that supports quality while encouraging environmental consideration. This is particularly critical given the decisive influence governments exert on companies, especially through taxation.

2.3 Clay in France

Between all different SCMs standards authorize, it may be more efficient to use clay in France as a result of its unlimited availability compared to other products. Indeed, clay is a promising material since it is geologically abundant, its calcination is low-cost, low-carbon and a simple process.

2.3.1 Availability

In France, clay has long been a fundamental resource, not only in traditional pottery and ceramics but also in modern construction, where it serves as a key component in bricks, tiles, and other building materials.

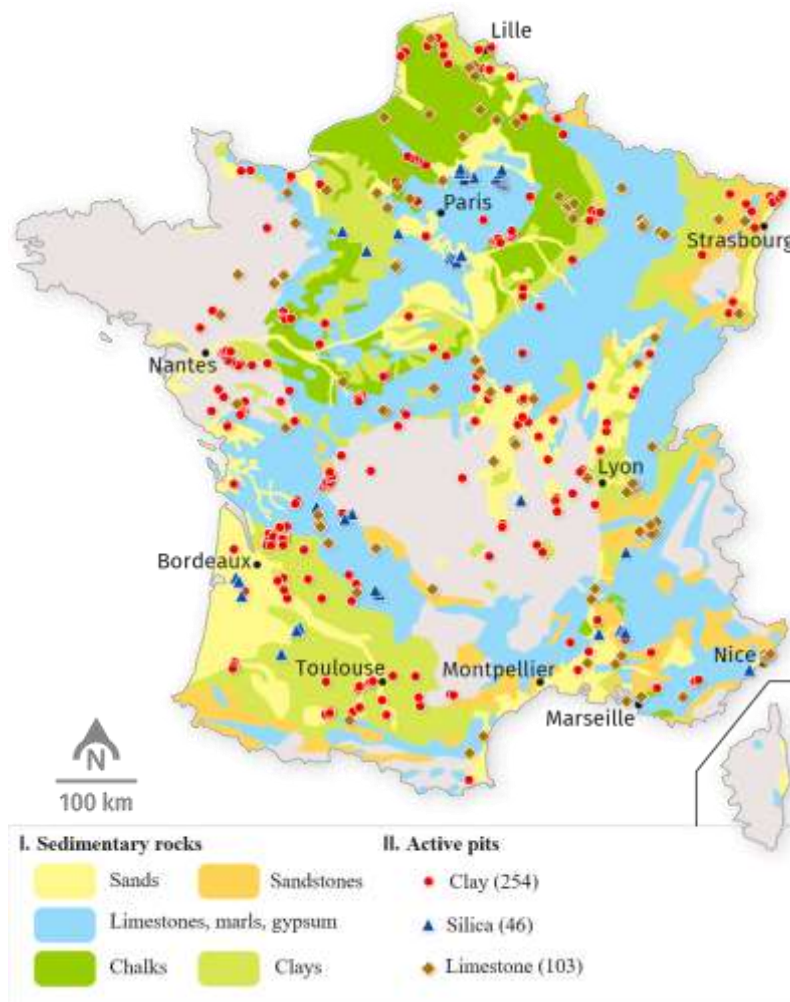


Figure 2.4 Simplified lithology map of France in 2015.

(BRGM, 2018)

The territory holds significant clay resources, but unfortunately, only a small portion is utilized by the cement industry. Most of the clay is used in the paper, ceramics, and earthenware industries, as well as in the production of glass, roof tiles, and bricks. The market is predominantly European, with a commercial surplus of 10.05 million euros in 2017. (BRGM, 2018).

However, clay product production has been declining over the years. For example, the production of terracotta materials fell by more than 25% between 2005 and 2014. (Haurine, 2015). This decline is due to increased taxation, such as the *redevance des mines*, and stricter policies that have led to the closure of many clay pits across the country. Additionally, innovations in construction products have reduced interest in traditional construction methods. As a result, traditional skills and expertise are disappearing, and these methods are no longer widely taught, leading to a lack of knowledge and trust in their use.

2.3.2 Reusing waste soils

While reopening clay pits has become very complicated due to policies and administrative complexities, waste clay can be a promising resource. Indeed, vast amounts of excavated soil are generated during construction projects, accounting for about 90% of urban waste. For example, the *Grand Paris Express*, one of the largest urban development initiatives in Europe, is generating an estimated 47 million tons of excavated materials. (Société du Grand Paris, 2022). Moreover, it is estimated that 80% to 90% of this excavated soil is an inert waste⁴ and can be reused in construction after minimal treatment. (Ministère de l'Environnement, de l'Energie et de la Mer, 2014). Consequently, the reuse of waste materials is scalable to major construction projects.

In response to this situation, various strategies for its reuse or disposal have been explored. Among them, the *Cycle Terre* project proposes to recycle unpolluted excavated soil for the construction of new neighbourhoods in Greater Paris. This project will explore all the

⁴ Inert waste is defined as “Any waste that does not undergo any significant physical, chemical or biological change, does not decompose, does not burn, does not produce any physical or chemical reaction, is not biodegradable and does not deteriorate the materials with which it comes into contact in a way likely to cause harm to the environment or health”. (Code de l'environnement - Article R541-8, 2016).

challenges of establishing an industry in an urban area, beginning with an exploratory phase to identify the major constraints and key factors necessary for setting up additional plants in the Paris suburbs. For instance, significant technical and regulatory challenges must be overcome. The variability in soil composition requires careful processing to ensure that the material meets construction standards, as well as considerations for transportation and intermediate storage. In this context, the project serves a demonstrative role, and its results will have a critical impact on the future of waste reuse in urban environments. (Gasnier, 2016).

Furthermore, raising awareness about the issue of excavated soil and its potential reuse has prompted political action. This is evidenced by the Grand Paris Express society's "défi des déblais", in which *Cycle Terre* was one of the winning projects, and the city of Paris's "Terres de Paris" exhibition. Such political support is crucial to adapt standards in good time, enabling the widespread adoption of these practices. (Loiret, 2021).

Moreover, although the initial investment in processing excavated soils may be significant, the long-term cost savings from reduced material transportation and waste management make this approach economically viable, not to mention the waste taxes avoided.

Finally, the stakes today are political, economic, environmental and cultural, with the potential to preserve local building traditions. However, it is important to recognize that earthen construction is not suitable for all projects. Therefore, innovations such as waste calcined clay cement should be developed to address these challenges, provided that they can be produced on an industrial scale.

2.4 Calcination energy consumption

2.4.1 Calcination process

Calcination is a thermal treatment process applied to materials like clay to induce changes in their chemical or physical properties. In the context of clays, calcination involves heating the material to a temperature typically ranging between 500°C and 900°C. The primary reason for calcining clay before alkali activation is to enhance its reactivity. Raw clay typically contains minerals such as kaolinite, illite, and montmorillonite. These minerals in their natural state are relatively inert and do not react effectively with alkaline solutions. Calcination dehydroxylates these clay minerals, breaking down the crystal structure and transforming them into more amorphous phases like metakaolin, which are highly reactive. This reactivity is crucial for the formation of a solid and durable geopolymer matrix during alkali activation. (Provis, 2018).

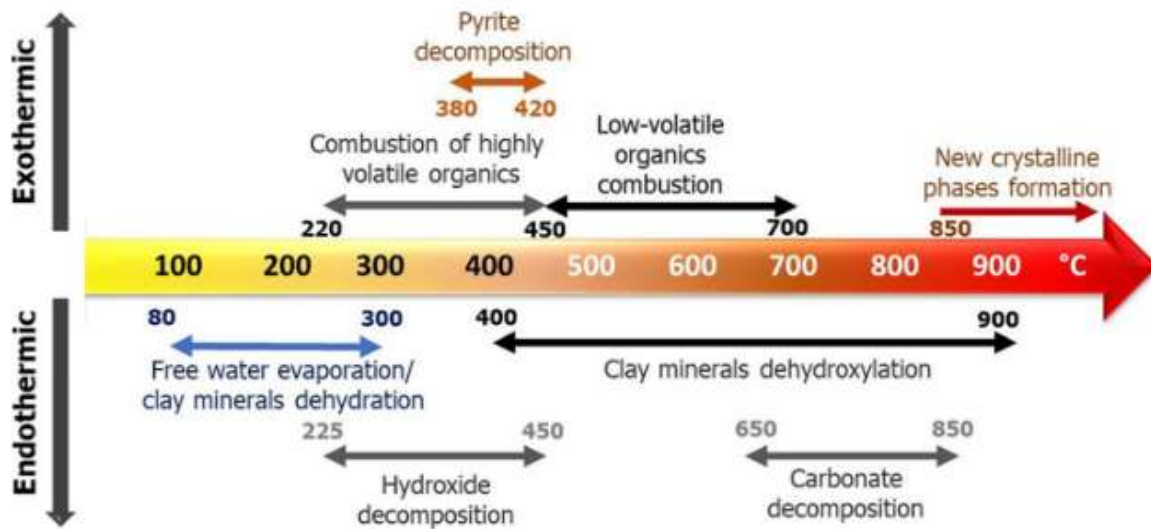


Figure 2.5 Typical reactions taking place during the calcination of clays in conventional calcination systems

(Hanein et al., 2022)

Moreover, the reactivity of clay is significantly influenced by its SSA, especially in the context of alkali activation. Changes in SSA can result from factors such as calcination temperature, duration, and the type of clay used. A high SSA generally enhances the reactivity of calcined clay, leading to more effective geopolymerisation. However, it also tends to increase water demand, which might negatively affect the workability and durability of the mix. Conversely,

a low SSA reduces water demand and improves workability, but this can come at the cost of reduced reactivity.

Therefore, the desired SSA must be carefully considered based on the objectives of the study. At an industrial scale, it's crucial to balance reactivity with practical considerations such as workability and application. (Boakye and Khorami, 2021).

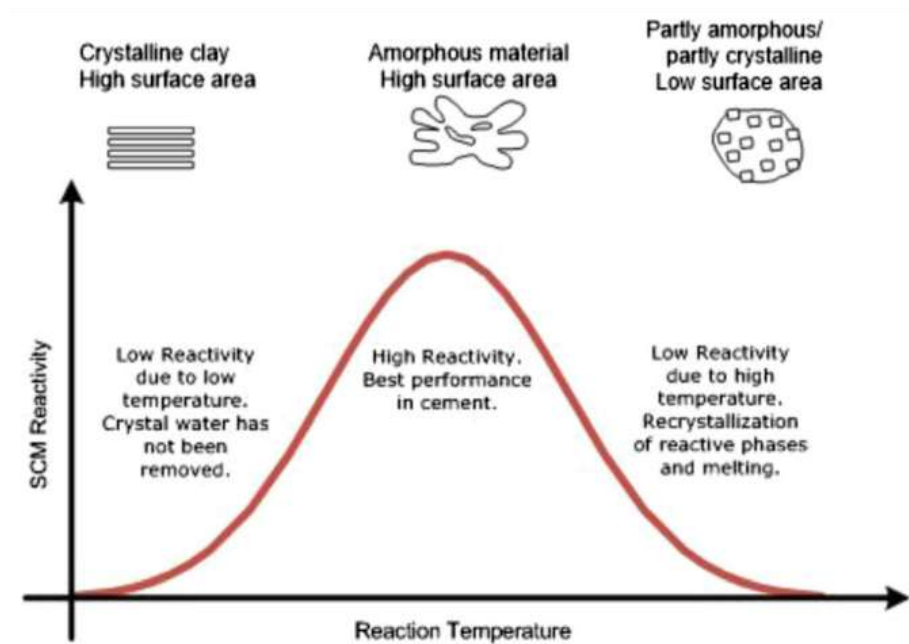


Figure 2.6 Simplified illustration of clay reactivity as a function of calcination temperature (Hanein et al., 2022)

Calcined clay serves as a crucial precursor in the alkali activation process. When mixed with an alkaline solution, such as sodium hydroxide or sodium silicate, the amorphous phases in the calcined clay react to form a geopolymer matrix. The extent of this reaction depends on the reactivity of the calcined clay, which directly impacts the strength development and durability of the final product. Higher reactivity generally leads to faster strength gain and more durable materials. For instance, the compressive strength of a mix with 20% cement replacement by calcined clay can be increased by 8% with a calcination temperature between 700°C and 800°C. (Boakye and Khorami, 2021).

2.4.2 Energy consumption

Although calcination is a decisive factor in the alkali-activation of clay, it is an energy-intensive process which may call into question its ecological interest. The temperature at which it is performed significantly impacts both the reactivity of the resulting product and the energy costs. The challenge is then to optimize the calcination temperature to balance these two factors.

Various studies have estimated CO₂ emissions and energy consumption of PC production. However, there is no standardised methodology or official data. Indeed, it depends on several factors, such as factory's geographic location, climate, type of kiln used or even the moisture content of the raw materials. (Atmaca and Yumrutaş, 2014). However, it is generally admitted that calcination of clinker consumes around 3 to 4 GJ/ton of clinker. This lack of centralised data complicates comparisons between cement production methods. Additionally, very few studies focus on calcined clay, often omitting some elements necessary for a comprehensive assessment. (IEA, 2018).

In this section, we will focus on the study conducted by X. Qian et al. in 2023, which compares the energy consumption of three cementitious materials with similar compressive strength, using Life Cycle Assessment (LCA) method⁵:

- Standard Ordinary Portland Cement (OPC) conforming to EN 197-1;
- Limestone Calcined Cement (LC³) composed of 50% OPC, 30% CC, 15% LS and 5% gypsum;
- Partially Calcined Limestone-Calcined Clay (PCL-CC) composed of 18% OPC, 53% CC, 27% partially calcined LS and 2% gypsum.

To evaluate the energy consumption of the calcination process, the study considered temperature and residence time for each material:

- OPC: 1450°C for 20 to 30 minutes (not explicitly stated in the study);
- CC: 800°C for more than 2 hours;
- PCL: 950°C for 10 minutes.

⁵ LCA considers the process of environmental load and their life cycle products, and is the most widely used methodology. (Qian and Ruan, 2023).

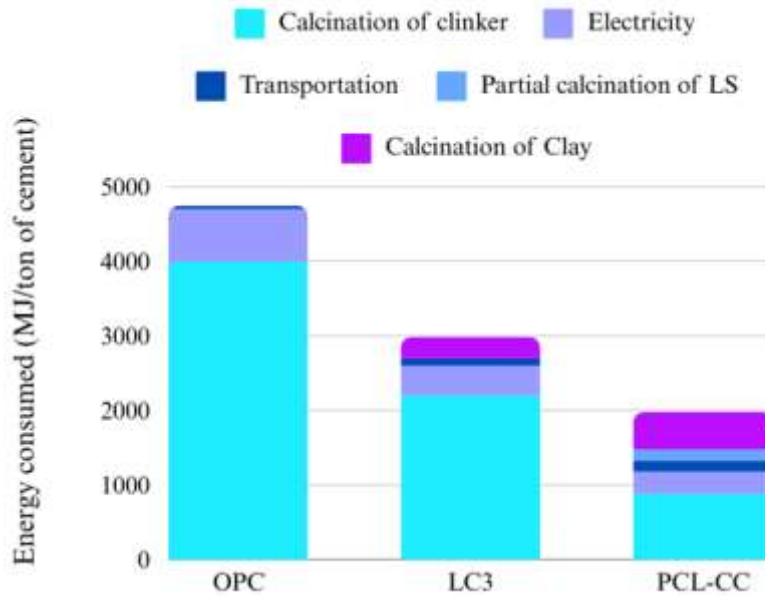


Figure 2.7 Energy consumption of three cementitious materials.

(Qian and Ruan, 2023)

The results, as illustrated above, indicate significant differences in energy consumption among the three materials, with OPC having the highest consumption, as expected. The data shows that the lower the clinker content, the lower the energy consumption. This aligns with the well-known fact that clinker is the most energy-intensive and polluting component of cement. Although the study does not provide specific data on calcined clay (CC) alone, it notes that for a ton of PCL-CC (which contains 53% CC), the energy consumption due to clay calcination is only 507 MJ. In contrast, for a ton of LC3 (which contains 50% OPC), the energy consumption due to clinkerization is 2200 MJ. While these two figures are not directly comparable, it is evident that the energy required for clay calcination is significantly lower than that for clinkerization. The study concludes that PCL-CC reduces energy consumption by 58.3% compared with OPC, while maintaining the same compressive strength. (Qian and Ruan, 2023).

In addition to that, calcination induces an energy loss estimated at 30 to 40% for rotary kilns, which are the most widely used system in the industry. This so-called waste heat occurs due to the temperature difference between the kiln's inner surface and the ambient air, leading to heat transfers through conduction, convection, and radiation. Naturally, this energy loss is more pronounced for clinker, which requires a higher calcination temperature than other materials like clay. (Atmaca and Yumrutaş, 2014).

Given the energy costs associated with calcination, ongoing research seeks to optimise the process. Some approaches include the use of alternative calcination methods, such as fluidised bed systems, which offer potential benefits in terms of energy savings. However, the complexity of implementing this system at an industrial scale makes it less feasible as an alternative for calcination. Nevertheless, the use of alternative fuels like biomass in the cement industry shows promise. (Hanein et al., 2022).

Thus, the use of calcined clay as the major component of cement emerges as one of the most viable strategies in the concrete industry. This approach is effective as long as the temperature and duration of calcination are carefully optimised to balance reactivity with energy consumption.

3. Research methodology

3.1 Research approach

The project aims to explore several challenges while remaining relevant to the construction industry:

- Considering the impure composition of waste clay, few studies have been conducted on its utilisation. Although alkali-activation of materials has been widely studied, most research focuses exclusively on metakaolin. Therefore, the first objective of this project is to assess the potential of alkali-activating waste calcined clay.
- Then, while cement can be produced using various materials, the transition from small-scale to large-scale production presents significant challenges. Only a few materials can be manufactured in ton-scale quantities, which is crucial for practical application. Additionally, it has to respect the standards of both EU and French government. Consequently, this project aims to evaluate the feasibility of producing alkali-activated waste calcined clay on an industrial scale.
- Finally, keeping in main the main objective of developing a low carbon cement, this project aims to explore ways to reduce the energy consumed during the calcination of clay. The critical question remains: can we achieve a balance between low energy consumption and cement performance performance ?

3.2 Materials

Given the limited timeframe for this project, only a few materials were studied: two types of calcined clay and one type of raw clay.

3.2.1 Calcined clays

The calcined clays used in this study were sourced from a previous project conducted at the University of Dundee. These clays, referred to as CC2F and CC9F, were reclaimed from interburden and overburden layers within existing Portland limestone quarries. They were

flash-calcined at 850°C as part of the earlier project, so no additional calcination experiments were conducted in our study.



Figure 3.1 Test reclaimed clay: prior and post calcination and ground

(Jones, Newlands, McCarthy and Hope, WOCA 2024)

3.2.2 Raw clay

The raw clay, known as FPC clay, was obtained during the project. It was pre-ground and ready for use upon arrival. Experiments were conducted to explore the effects of temperature on this clay.



Figure 3.2 Ashing furnace used to calcine FPC clay

3.2.3 Alkaline solution

The activating solutions were prepared based on the work of John Provis on metakaolin, which provides insights into the influence of the microstructure of geopolymers on their mechanical properties. (Duxson and Provis, 2005).

The activating solutions consisted of sodium hydroxide (NaOH), silica (SiO₂) and water, with the following ratios:

$$\text{Si/Al} = 1.9 \text{ in the mix}^6;$$

$$\text{SiO}_2/\text{Na}_2\text{O} = [0;2] \text{ in the solution.}$$

The amount of water was initially intended to give a w/c ratio around 0.4 but was adjusted according to the consistency of the mix. The solutions were then stored for a minimum of 24 hours prior to use to allow for equilibration.

3.3 Characterisation methods

The experimental strategies were inspired by previous work on metakaolins. We focused on the fundamental characterisation of each clay in order to evaluate the feasibility of the process.

3.3.1 X-Ray Fluorescence (XRF)

The XRF test is an analytical technique used to determine the elemental composition of materials. It was conducted on CC2F, CC9F, FPC and nine calcined variations of FPC. The purpose of this test was to identify the main components of the clays that will react with the activating solution.

⁶ The mix refers to the activating solution mixed with the calcined clay.



Figure 3.3 PANalytical Zetium XRF instrument

3.3.2 X-Ray Diffraction (XRD)

The XRD test is a quantitative technique that provides detailed information about the crystalline structure of the material. In particular, it analyses the diffraction pattern of x-rays passing through the crystals. In our study, it was used to determine the quartz content in the clay, as quartz is a crystalline mineral primarily composed of silica.

These two first methods allow us to determine the relevant composition of alkaline solution according to suggested ratios, considering amorphous elements only.



Figure 3.4 Siemens D5000 XRD instrument

3.3.3 Laser Diffraction Particle Sizing (LD)

The LD is a method used to determine the particle size distribution of materials. It is based on the diffraction of a laser beam by a dispersed group of particles in a medium such as air or liquid. Particle size distribution is critical as it influences material properties like flowability and reactivity, which are especially important in the context of the project.



Figure 3.5 Malvern Mastersizer2000 Laser diffractometer (left) using a Hydro2000MU dispersion unit and water as dispersant. (right)

It also provides information about the external surface area of the material, based on the PSD data. Since this is an estimation that does not consider the internal surface area within pores, the values can be significantly lower than those obtained from the BET technique, which measures both external and internal surface areas

3.3.4 Brunauer, Emmett and Teller Technique (BET)

The BET technique is used to determine the specific surface area of solids and powders, reported in units of area per mass of sample (m^2/g). SSA is a significant property of clay as it affects its reactivity and water demand. In our study, BET analysis was conducted on FPC to evaluate changes in SSA due to calcination.



Figure 3.6 Anton Paar Nova800 specific surface area analyser

3.3.5 Automatic Vicat Apparatus

The Vicat instrument is used to determine the setting time of cement. By measuring the penetration of a needle into the cement paste, the instrument provides information about the initial and final setting times, which are key parameters in cement development. This test was conducted on CC2F and CC9F to evaluate the reactivity of the mixes, and the results were instrumental in selecting the ratios for the activating solution.

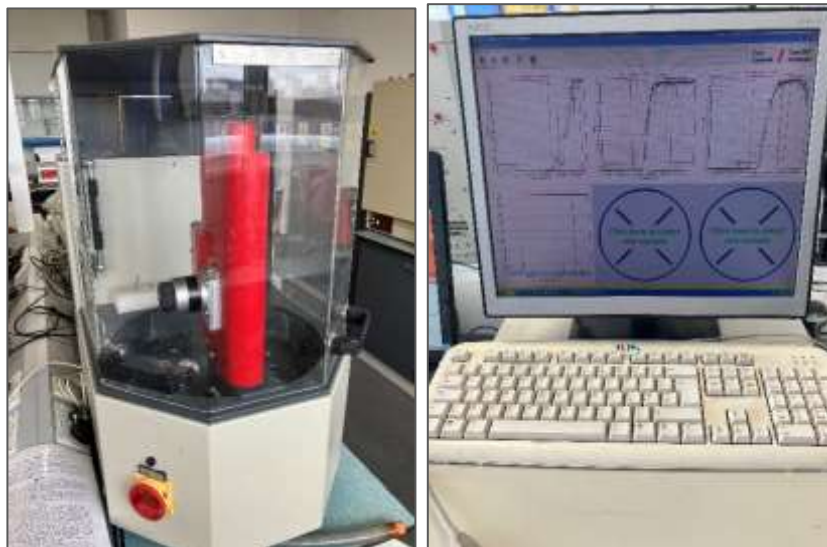


Figure 3.7 ToniSet Compact automatic Vicat instrument and software

3.3.6 Compressive Strength Testing

Compressive strength tests were conducted on two 50 mm cement cubes made from CC2F and CC9F at 1, 3, 21 and 34 days. The tests were performed using a base load of 0.5 kN and a loading rate of 2.4 N/s, with a target failure rate of 10%. These parameters were selected to evaluate the early-age strength development of the alkali-activated materials.

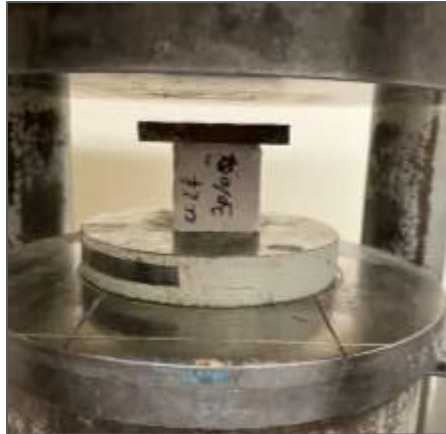


Figure 3.8 CC2F in the load frame before testing, 26/08/2024

3.3.7 Carbonation Testing

The carbonation test is intended to determine the extent of CO₂ infiltration into the concrete, which directly impacts its durability. The test was conducted under controlled conditions with a CO₂ concentration of 4%. This level of CO₂ exposure was used to simulate the long-term effects of atmospheric carbonation on the material. Given that carbonation can lead to the corrosion of embedded steel in reinforced concrete, this test is crucial for understanding the durability of the alkali-activated materials.



Figure 3.9 Carbonation tank gas concentration controller

4. Results and discussion

This project is divided into two parts, so the results will be discussed accordingly. First, the results for CC2F and CC9F will be presented, covering their characterization through to the strength tests, followed by a discussion of the FPC calcination experiments through its structural analysis.

4.1 CC2F and CC9F

4.1.1 X-Ray Fluorescence (XRF)

Before conducting any testing, it was essential to determine the elemental composition of our calcined clays, which are presented in the table below:

Table 4.1 XRF results for CC2F and CC9F⁷

Sample	CC2F	CC9F
Element	Proportion (wt%)	Proportion (wt%)
<i>SiO₂</i>	53.779	60.065
<i>Al₂O₃</i>	34.651	22.934
<i>Fe₂O₃</i>	2.198	8.748
<i>K₂O</i>	4.584	1.213
<i>MgO</i>	0.372	0.993
<i>F</i>	0.226	-
<i>Na₂O</i>	0.189	0.157
<i>CaO</i>	0.161	2.353
<i>TiO₂</i>	0.153	1.261
<i>SO₃</i>	-	0.128
Total	96.313	97.852

As expected, our waste clays contain elements that can be considered impurities, as opposed to metakaolin. However, the major components — SiO_2 and Al_2O_3 — are consistent with those typically found in metakaolin. Notably, there are significant amounts of Fe_2O_3 , K_2O , and CaO . While the roles of these additional components in alkali activation are not yet fully understood, we focused on the primary components (SiO_2 and Al_2O_3) for alkali activation, specifically to determine the Si/Al ratio.

⁷ Elements with a proportion inferior to 0.1% of the sample mass are not represented in this table. (Appendix 2).

It's important to remember that waste clays do not have a uniform composition. To ensure the relevance of this project, we compared our samples with other waste calcined clays. Fortunately, the compositions of our two clays are similar to those found in other studies. For example, a study on the reuse of clay brick powder, typically made from common clays, analyzed 20 different materials. (*Appendix 3*).

They found an average composition of:

SiO₂: 62.69 %

Al₂O₃: 16.40 %

Fe₂O₃: 5.74 %

Although the exact values differ, the general trends are similar to those of CC2F and CC9F. Therefore, we can confidently use the XRF data in the subsequent stages of this study. However, it is crucial to remember that not all elements are present in their amorphous phase, which is why an XRD test is also indispensable.

4.1.2 X-Ray Diffraction (XRD)

The mineral and chemical compositions of calcined clays are closely related to their reactivity, making XRD analysis necessary. XRD identifies crystalline phases, such as quartz, muscovite, and illite, which are typical components of clays.

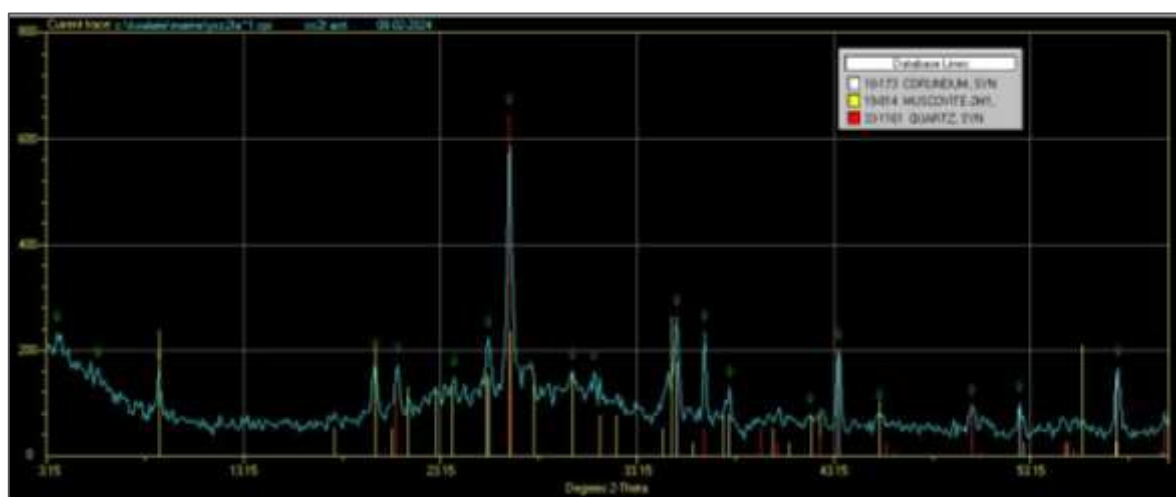


Figure 4.1 XRD result for CC2F.

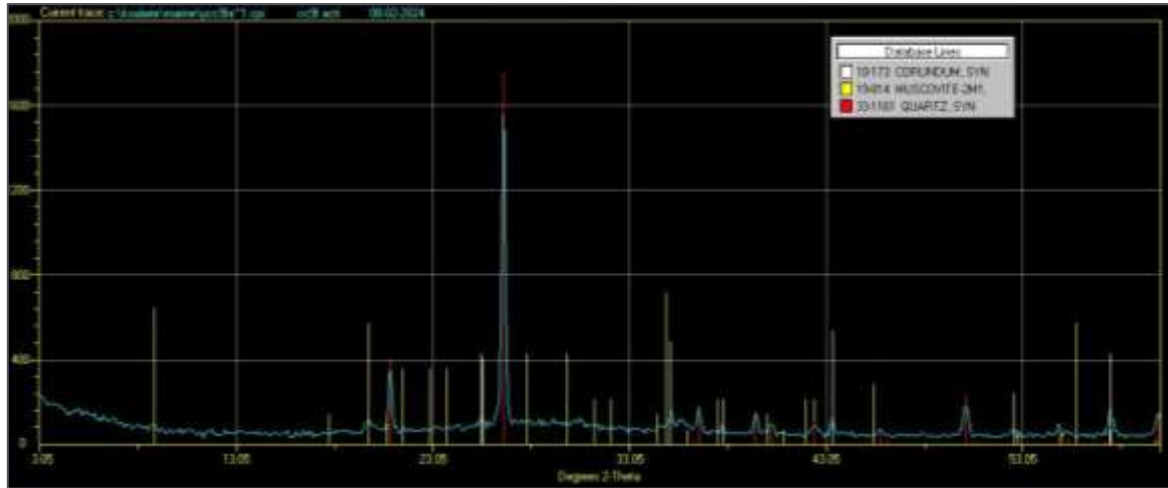


Figure 4.2 XRD result for CC9F.

As expected, the most prominent peak corresponds to quartz, the primary crystalline mineral in clays, primarily composed of SiO_2 . However, other crystalline elements may be more challenging to detect with this technique due to the limitations of XRD as a qualitative method. CC2F and CC9F contain approximately 14% and 28% quartz, respectively. Additionally, their amorphous phase content is 40% and 35%, respectively. This suggests that slightly less than half of the clay is reactive, which is significant for alkali activation.

4.1.3 Ratio calculation

Based on the previous findings and experiments, we determined the composition of the activating solution. We initially tested a Si/Al ratio of 1.9 and an $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of 1.5 to observe the reaction. The second ratio was then adjusted. According to John Provis's work, a Si/Al ratio of 1.9 is crucial for maximizing cement strength, while the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio can vary depending on the material. Below is a summary of the different ratios tested for both CC2F and CC9F:

Table 4.2 Summary of the ratios tested on CC2F and CC9F.

<i>Si/Al</i>	1.9						1.8	1.9	2.0
<i>SiO₂/Na₂O</i>	1.2	1.4	1.6	1.8	2.0	2.2	1.7		

Notably, the w/c ratios were quite different between CC2F and CC9F, at 0.7 and 0.4, respectively. While the first ratio seems unusually high, it represents the minimum amount of water necessary to create a workable cement paste. This highlights a key difference in the behavior of alkali-activated calcined clay compared to Portland cement.

Despite these w/c ratios, mixing the paste proved challenging, as it does not behave like a Newtonian fluid but as a Bingham one. Thus, the paste required mechanical agitation to flow, indicating that the use of a shaking table could be beneficial for ensuring proper mixing and flow in the molds.

4.1.4 Setting times

All mixes were tested using the AutoVicat instrument. After evaluating the mixability of the pastes, setting times became a decisive factor in selecting the appropriate ratios for future compressive strength and carbonation tests. The graphs with Si/Al = 1.9 and SiO₂/Na₂O = [1.2; 1.4; 1.6; 1.8; 2.0; 2.2] are presented below:

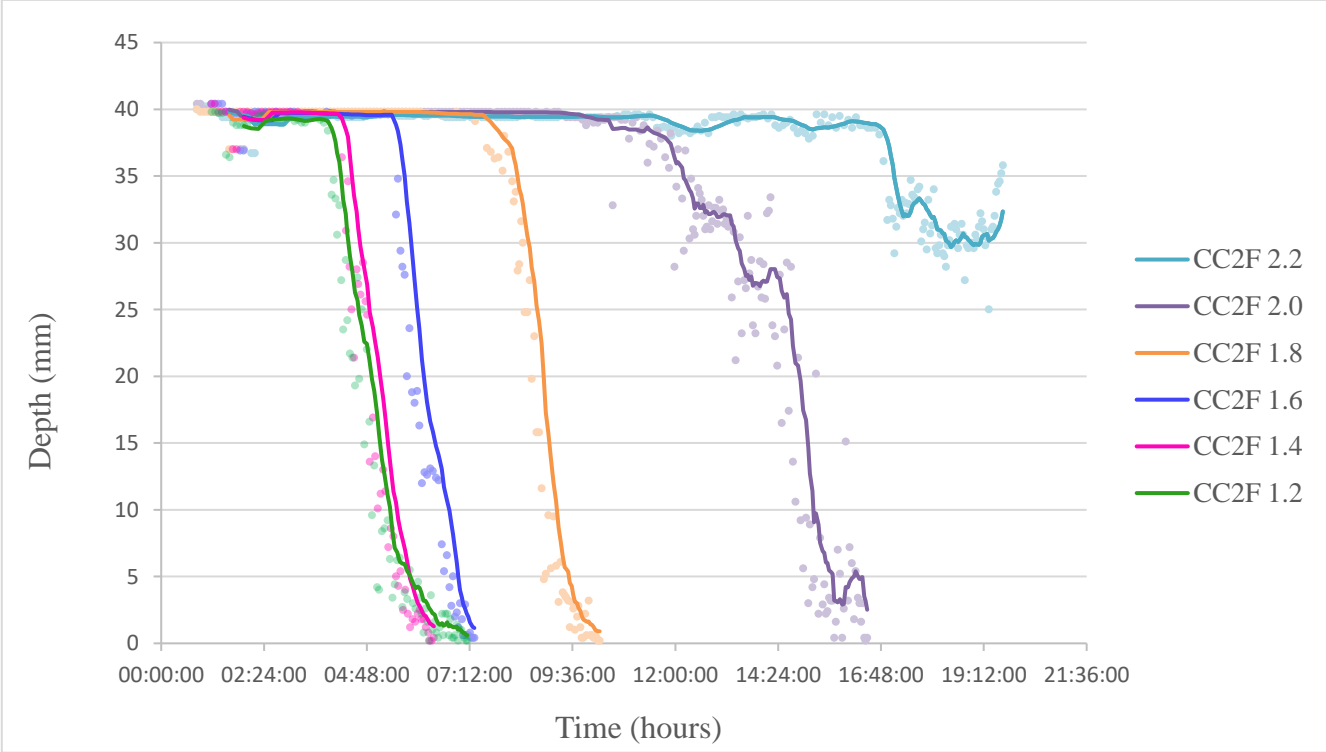


Figure 4.3 Setting times of CC2F with Si/Al=1.9 and different alkali-ratios.

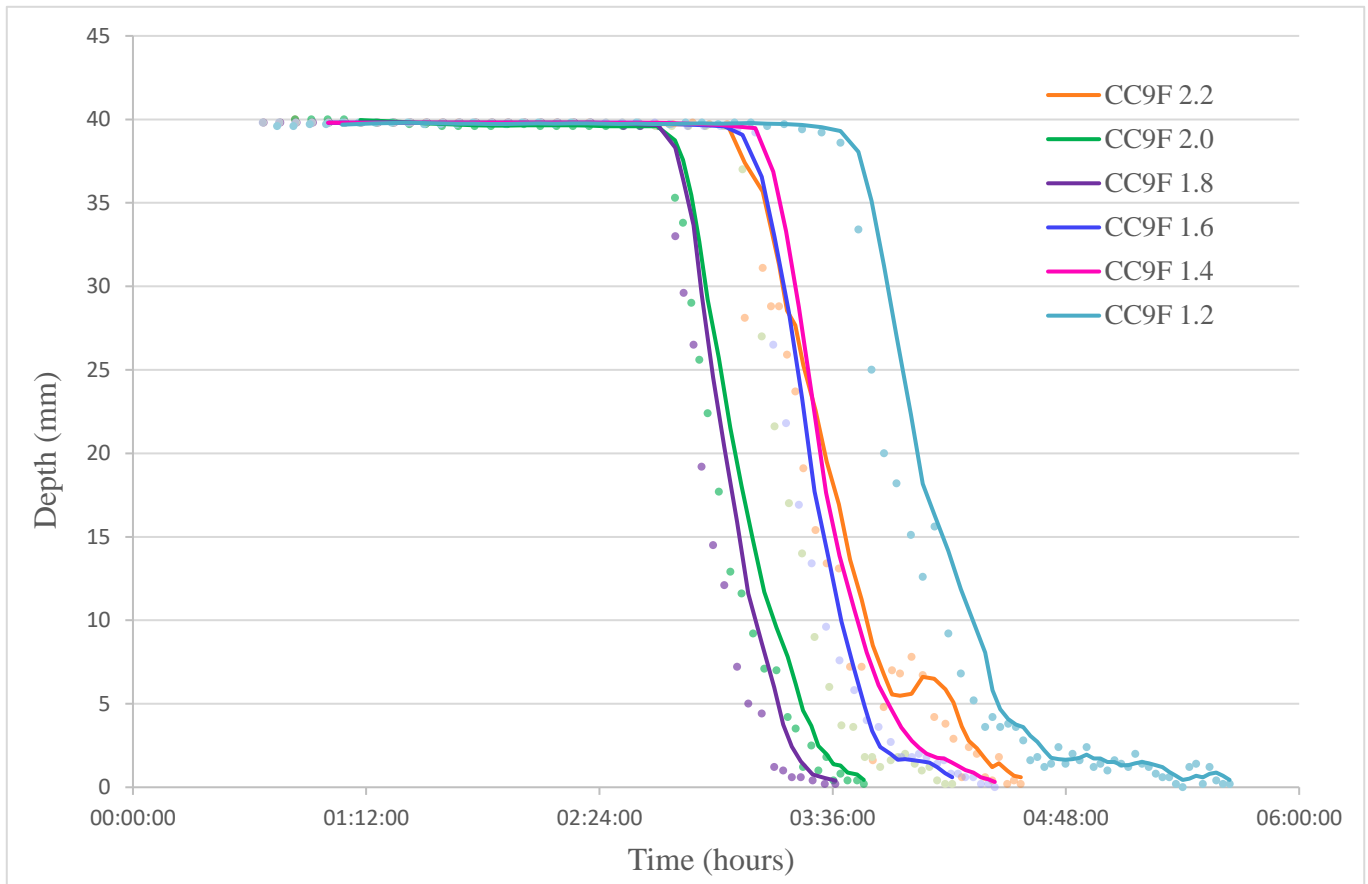


Figure 4.4 Setting times of CC9F with Si/Al=1.9 and different alkali-ratios

The most striking observation is the average difference in setting times between the two clays. The CC2F paste begins setting between 4 and 12 hours (a significant range), while the CC9F paste starts setting between 3 and 4 hours. In other words, CC9F is fully set by the time CC2F begins to activate.

For CC2F, setting time generally increases with higher alkali ratios; however, the CC9F paste does not follow the same pattern, as the curves are close together and not in a rising order. Notably, the 2.2 alkali-ratio mix for CC2F does not even set, indicating instability at higher ratios. Instability is also observed in CC2F at alkali ratios of 2.0 and 2.2, and in CC9F at ratios of 1.2 and 2.2. This suggests that extreme alkali ratios may not be optimal.

To maintain a setting time between 4 and 8 hours, CC2F alkali ratios of 1.2, 1.4, and 1.6 are suitable, while all CC9F ratios, except for 1.8 and 2.0 (which are too fast), fall within this range. It is essential to remember that concrete requires sufficient time to be mixed, transported, and placed at the construction site. That is why the 4 to 8-hour window is often considered optimal for balancing workability and progress of the construction project.

For consistency and comparability in subsequent experiments, we chose an $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of 1.7 for both calcined clays. The goal was to identify a common alkali ratio suitable for all waste calcined clays. However, it was evident that CC9F activates too quickly; one hypothesis for this behavior is the high proportion of iron, which accounts for 8%, in CC9F, compared to only 2% in CC2F. As a matter of fact, iron can affect both characteristics and performance of the clay, such as its rheology, calcination process, strength gain, water demand or also setting times. To test this hypothesis, we conducted additional setting time tests by varying the Si/Al ratio and by adjusting the ratio to account for the iron content, considering 50% of the iron as acting similarly to alumina.⁸ In this scenario, the ratio becomes $\text{Si}/(\text{Al} + 0.5\text{Fe})$. The results are shown below.

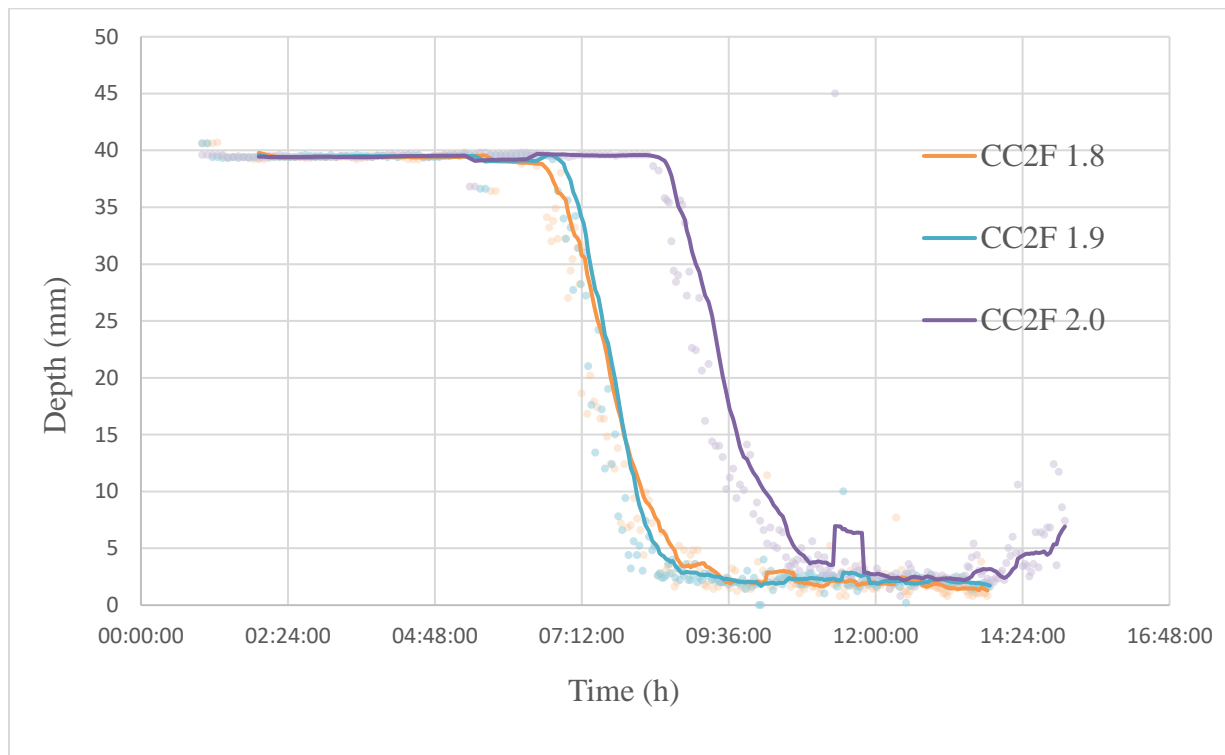


Figure 4.5 Setting times of CC2F with $\text{SiO}_2/\text{Na}_2\text{O}=1.7$ and different Si/Al ratios.

⁸ This proportion was proposed by Prof. Jones and is purely arbitrary. That way, it may not be the most accurate figure.

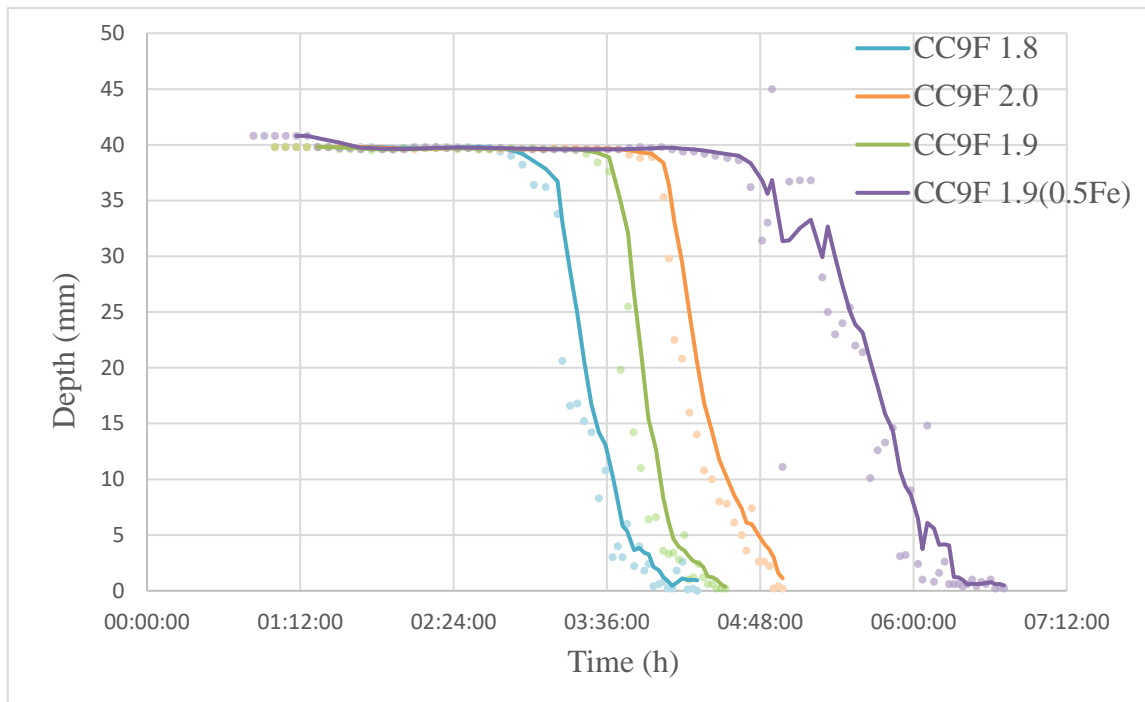


Figure 4.6 Setting times of CC9F with $\text{SiO}_2/\text{Na}_2\text{O}=1.7$ and different Si/Al ratios.

The results are intriguing. On the one hand, the activation time increases with a higher Si/Al ratio, although the 1.8 and 1.9 ratios for CC2F are quite similar. On the other hand, considering 50% of the iron as alumina significantly alters the setting time, increasing it by 1 hour (initial) and 1.5 hours (final). This adjustment results in an activation time between 4 and 6 hours, which is more suitable for industrial applications. It is evident that iron plays a role in the activation of calcined clay when present in high proportions, requiring further research.

In conclusion, we decided to use $\text{Si}/\text{Al} = 1.9$ for the rest of the project, as recommended by John Provis's study, and to keep $\text{SiO}_2/\text{Na}_2\text{O} = 1.7$

4.1.5 Compressive strength

Compressive strength test were performed on two samples, one from CC2F and one from CC9F. Their characteristics were:

$$\text{Si}/\text{Al} = 1.9 \text{ (without considering the iron in both cases}^9\text{)}$$

⁹ Given that experiments were to be conducted at 1, 3, 21 and 34 days, the iron hypothesis was not approved yet so we preferred to keep the initial ratios.

SiO₂/Na₂O = 1.7



Figure 4.7 CC2F and CC9F before strength test

Experiments were conducted on two cubes of 50 mm with the parameters previously presented and illustrated below:

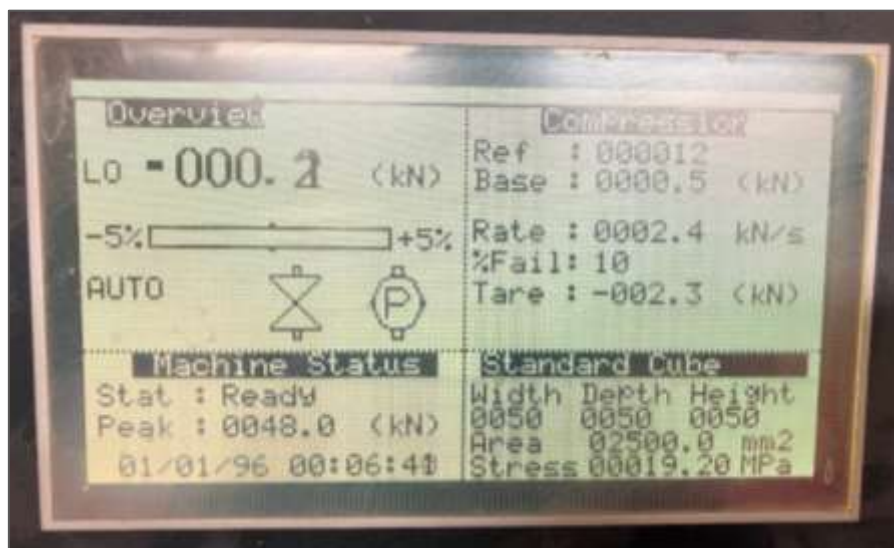


Figure 4.8 Compressive strength parameters.

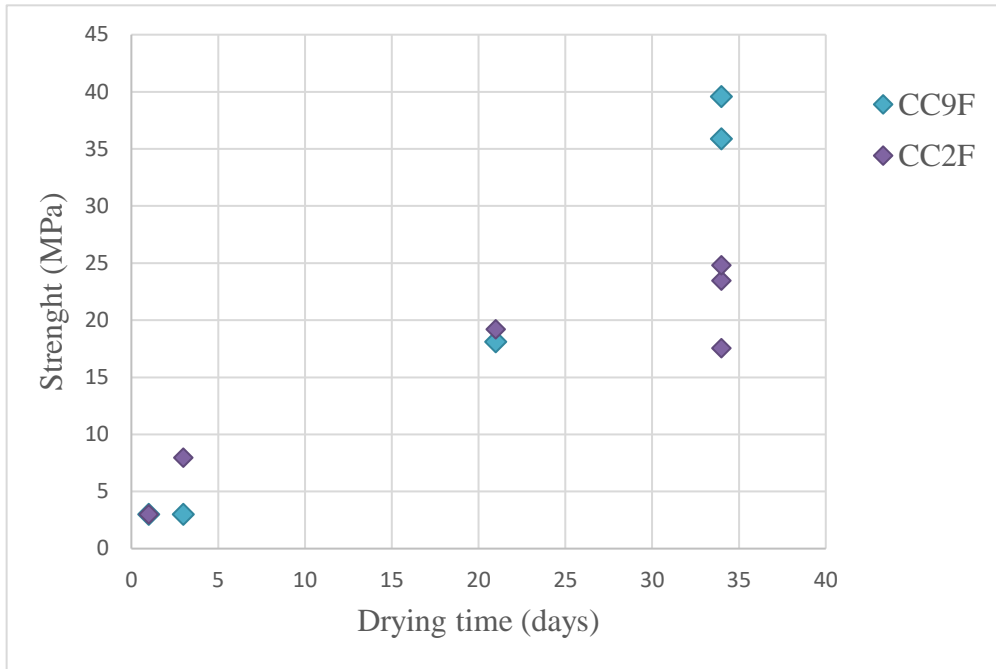


Figure 4.9 Compressive strength of CC2F and CC9F at 1, 3, 21 and 34 days.

The test revealed that the initial compressive strength was poor, with the cubes behaving more like sandcastles under compression. However, at 21 and 34 days, CC9F improved strength and performs better than CC2F. Indeed, the compressive strength of the latter was roughly similar after 14 days, which is the behaviour expected for this material.



Figure 4.10 CC2F (left) and CC9F (right) normal failure at 34 days.

It's important to note that these results are preliminary and should not be compared directly with conventional mortar or concrete compressive strengths due to the differences in test conditions and materials. As a matter of fact, cement paste is a difficult material to measure strength, it is then preferable to use aggregates to obtain more relevant results.

4.1.6 Carbonation

The carbonation test was conducted to assess the resistance of CC2F and CC9F¹⁰ samples to CO₂ infiltration, which is crucial for understanding long-term durability.

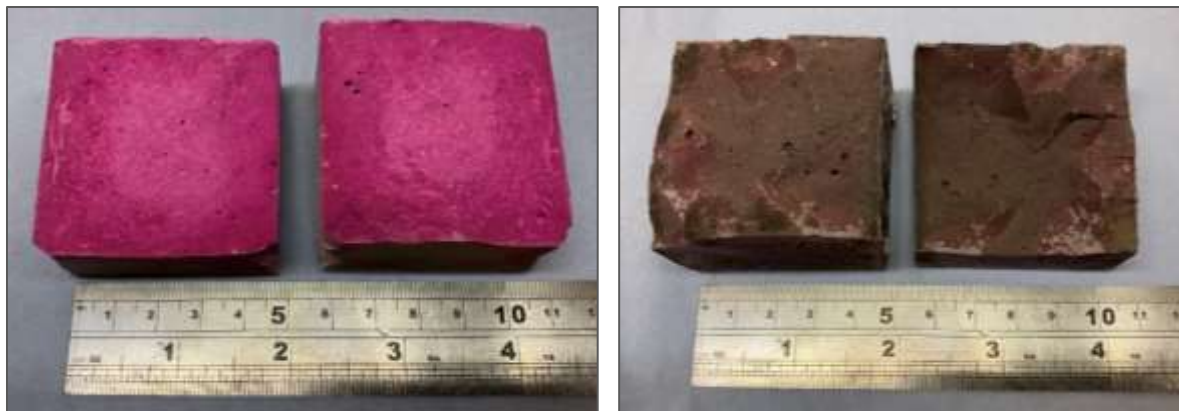


Figure 4.11 CC2F (left) and CC9F (right) split surface after carbonation test.

The results showed that CC2F performed well, with visible pink coloration indicating minimal carbonation. However, CC9F, due to its darker natural color, was harder to assess, although some pink areas were observed, suggesting that it was also not fully carbonated.

This finding is significant, as it indicates that CC2F may be more suitable for use in concrete, while CC9F's high iron content might be affecting its activation and carbonation resistance, warranting further investigation.

¹⁰ This sample of CC9F takes account of iron's behavior.

4.1.7 General observations

Several challenges and observations were noted during the experiments:

Mixability Issues:

Both CC2F and CC9F pastes presented significant challenges in mixing, with CC2F being particularly difficult. These pastes showed a high water demand that was not predictable prior to testing. The process of determining the optimal w/c ratio proved challenging. Initially, we started with a w/c ratio of 0.3, but despite gradually adding more water, mixability barely improved. For instance, in the case of CC2F, a noticeable improvement in mixability was only observed when the w/c ratio reached 0.6, which is significantly higher than what is typically required for traditional cement.

Moreover, the relationship between water addition and mixability was non-linear; even a small increase in water content could suddenly and drastically alter the paste's texture. This erratic behavior is a common issue with materials like these and is likely related to their high SSA, which increases water demand, or to their Bingham fluid behavior. Unfortunately, due to the unpredictable nature of this issue, we were unable to identify a reliable solution during the tests.



Figure 4.12 CC2F mix.

Besides attempts to use plasticizers did not improve the mixability, suggesting that the chemical interaction between plasticizers and calcined clays differs from that with Portland cement.

Bleeding:

Bleeding was observed, a common issue in cement production. Although it did not appear to impact the study, solutions typically used for Portland cement may not be effective for calcined clays.

Activating-ratios:

Although we chose to use a common activating ratio of $\text{SiO}_2/\text{Na}_2\text{O} = 1.7$ for the compressive strength and carbonation tests, it is important to recognize that this ratio may not be optimal for both types of clay, particularly for CC9F. The reason behind this choice was to simplify comparisons across the different clays, as the goal was to identify a standard ratio for evaluation. Additionally, this ratio was selected because its performance was representative of the average results observed across other tested ratios.

Cracking:

Cracking occurred in early CC2F samples, possibly due to the high water content. It can lead to excessive shrinkage during drying, as the water evaporates and the material contracts. This shrinkage can cause tensile stresses to develop within the material, leading to cracking. However, it was not possible to reduce the amount of water. Although this issue did not persist, the cause remains unclear.

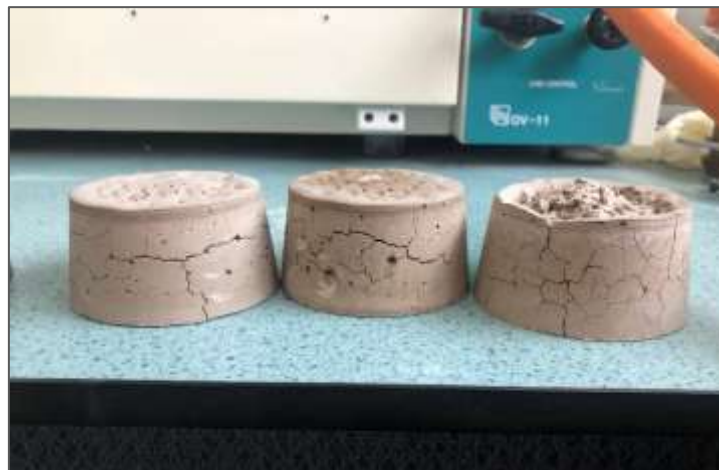


Figure 4.13 CC2F cracked samples.¹¹

¹¹ This picture illustrates samples after experiment with the AutoVicat instrument. Indeed, cracking here is probably due to the needle which kept breaking the paste during few hours of testing.

Unexpected Fracture:

When removing first CC9F cubes from their molds, some broke in an unusual vase-like shape, possibly during the initial drying phase.



Figure 4.14 CC9F cubes broken in a vase shape.

Possible issues can include:

- Improper drying: it may lead to unexpected or irregular cracking when it is handled, probably because it may not have developed sufficient strength when drying;
- Inadequate framework: it might be too tight or not properly aligned, causing stress concentrations or uneven pressure on the cement cube, leading to an unusual cracking pattern. However, this hypothesis is highly unlikely in this context, as it has occurred on several occasions and only with CC9F samples.

We reviewed the process but nothing came of it. However, the last samples of CC9F were realised considering 50% of iron, and, surprisingly, they were not broken when removed from the mould. This supports the hypothesis that iron plays a significant role in the alkali-activation process.

To conclude, these observations highlight the unique challenges of working with calcined clays and suggest areas for future research, particularly in improving mixability and understanding the role of iron in the activation process.

4.2 FPC

4.2.1 Calcination

Before conducting any experiments, it was necessary to calcine the clay. Therefore, decisions about the calcination parameters were required. A previous project conducted at the University of Dundee demonstrated negligible differences between flash and rotary calcination regarding fresh properties, compressive strength, and reactivity. Consequently, we decided to use flash calcination for the following reasons:

- Flash calcination was more practical for the small amount of clay we needed to calcine.
- Flash calcination is less energy-intensive.
- Flash calcination had already been performed on CC2F and CC9F, allowing us to compare the three clays.

However, it is important to note that although flash calcination is less energy-intensive than rotary calcination, the latter is widely used in industry due to its efficient heat transfer, which ensures uniform heating at high temperatures and enables large-scale production. Therefore, while flash calcination was used for our project, rotary calcination would be more relevant for industrial-scale applications.

Given that the common calcination process for clays is typically done at 850°C, we found it relevant, in the context of energy savings, to compare three different temperatures: 650°C, 750°C, and 850°C. This comparison was conducted at three different durations: 20, 40, and 60 minutes. The table below summarises the parameters:

Table 4.3 Summary of calcination parameters for FPC.

<i>Temperature (°C)</i>	650			750			850		
<i>Duration (min)</i>	20	40	60	20	40	60	20	40	60
<i>Sample name</i>	a	b	c	d	e	f	g	h	i

After calcination, the samples were removed from the furnace and left to cool at ambient temperature (25°C). We began the process by calcining 30 g of FPC per sample to minimize waste.

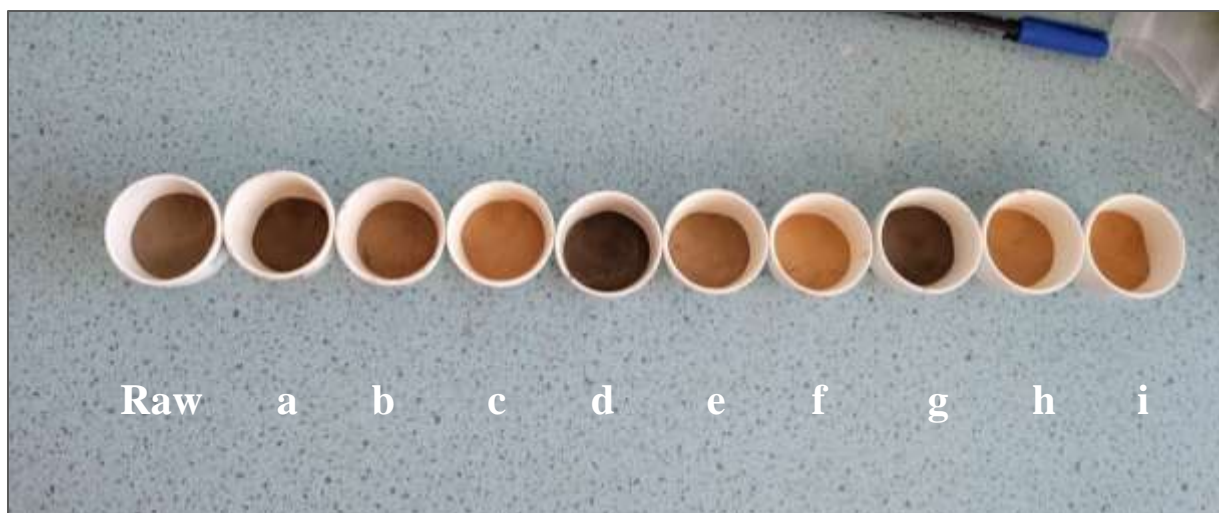


Figure 4.15 FPC samples after calcination.

Initially, the natural dark color of the clay is noticeable, indicating the presence of iron, which could potentially interfere with the alkali-activation process, as studied previously. The change in color during calcination is also evident; it is the duration of calcination — rather than the temperature — that gives the clay its reddish color (characteristic of Fe_2O_3). Since all the 20-minute samples appear similar in color to the raw clay, it is assumed that there are minimal changes in their crystalline structure. As a reminder, calcination is crucial in the alkali-activation process because it transforms the crystalline structure into an amorphous one, among other changes (such as improved reactivity and dissolution properties).

However, upon blending, we observed that only the thin surface layer of the samples had changed color. This observation can be attributed to several factors, including the surface's exposure to heat and oxygen, which may induce oxidation during the process. This oxidation may be intensified by the rapid cooling of the sample. Indeed, the interior of the sample does not cool as quickly as the surface, which undergoes thermal shock upon removal from the oven. Iron, in particular, is sensitive to sudden temperature changes, which can influence its oxidation state and distribution within the sample. Therefore, the cooling cycle may be the key to the oxidation process, especially in flash calcination.

Besides, the difference in color indicates partial transformation, suggesting that the calcination process was incomplete. This incomplete calcination could negatively impact the reactivity and performance of the clay in subsequent applications. This is where a rotary kiln could prove more effective, as it ensures a more uniform calcination process. In contrast, flash calcination is best suited for thin layers of clay, making it challenging to scale up to industrial production levels.

4.2.2 X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD)

An XRF test was conducted on the raw FPC sample to determine its chemical composition. This test was not repeated for the other samples, as the calcination process used does not induce significant changes in the chemical composition of the clay. However, XRD tests were performed on each sample, as calcination alters the mineralogy of the product.

The results are presented below:

Table 4.4 XRF results for FPC raw clay.

<i>Element</i>	<i>Proportion (wt%)</i>
<i>SiO₂</i>	44.23
<i>Al₂O₃</i>	15.16
<i>Fe₂O₃</i>	6.40
<i>CaO</i>	9.93
<i>MgO</i>	2.93
<i>K₂O</i>	2.59
<i>SO₃</i>	1.27
<i>Ba</i>	1.00
<i>TiO₂</i>	0.76
<i>Na₂O</i>	0.48
<i>P₂O₅</i>	0.18
<i>MnO</i>	0.12
<i>Total</i>	85.06

As expected, the composition of FPC is similar to that of other clays, with a relatively high proportion of iron. However, while the proportions of Al₂O₃ and Fe₂O₃ are close to the previously presented averages —16.40% and 5.74%, respectively— the proportion of SiO₂ is quite low compared to the average of 62.69%. Consequently, its activating solution will probably contain a higher content of SiO₂ than the CC2F and CC9F solutions.

Table 4.5 XRD results for the 10 samples of FPC.

<i>Sample</i>	<i>raw</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>
<i>Quartz (wt%)</i>	20.35	19.91	24.36	24.59	31.79	23.34	20.57	35.76	30.44	25.15
<i>Amorphous (wt%)</i>	64.49	61.40	55.36	47.66	38.72	64.24	67.84	46.13	52.20	64.75

At first glance, the results may seem difficult to interpret as they reflect a complex behavior. We observe that during the initial phase of calcination, when the temperature is low (samples a, b, c) or during the first 20 minutes (samples d, g), the quartz content actually increases, leading to a corresponding decrease in the amorphous phase. This formation of quartz is accelerated at higher temperatures (samples d, g). Then, after 20 minutes at a high temperature (samples e, f, h, i), the quartz content starts to decrease, leading to an increase in the amorphous content. However, it is noteworthy that the amorphous content remains relatively constant, indicating various phase transformations throughout the process.

Overall, we can hypothesise that, over time, some components of the clay first crystallise, particularly the quartz, which initially increases in content before melting and contributing to the formation of the amorphous phase. This process appears to be accelerated by increasing temperature. Indeed, the calcination process at 650°C for durations under one hour is not suitable for alkali-activation, as the clay will not be sufficiently reactive.

4.2.3 Laser Diffraction (PSD)

Particle size distribution (PSD) analyses were performed on the series of FPC clay samples. The results indicate that the particle size distribution does not change significantly with different calcination processes. However, some trends were observed in the external SSA calculated from the PSD data.

The SSA generally decreases as the calcination temperature increases. However, when the samples are kept in the oven for longer durations, there is a slight increase in SSA. Therefore, the lowest SSA was observed for the sample calcined at 850°C for 20 minutes.

Table 4.6 SSA of FPC samples determined by LD (m²/g).

<i>Raw: 0.805 m²/g</i>	650 °C	750 °C	850 °C
<i>20 min</i>	0.610	0.571	0.495
<i>40 min</i>	0.637	0.580	0.529
<i>60 min</i>	0.658	0.579	0.535

Regarding particle sizes, both increased duration and temperature during calcination lead to coarsening, particularly noticeable in the smaller size fractions. This indicates that finer particles agglomerate or sinter together under higher temperatures and prolonged exposure. Representative graphs are provided below :

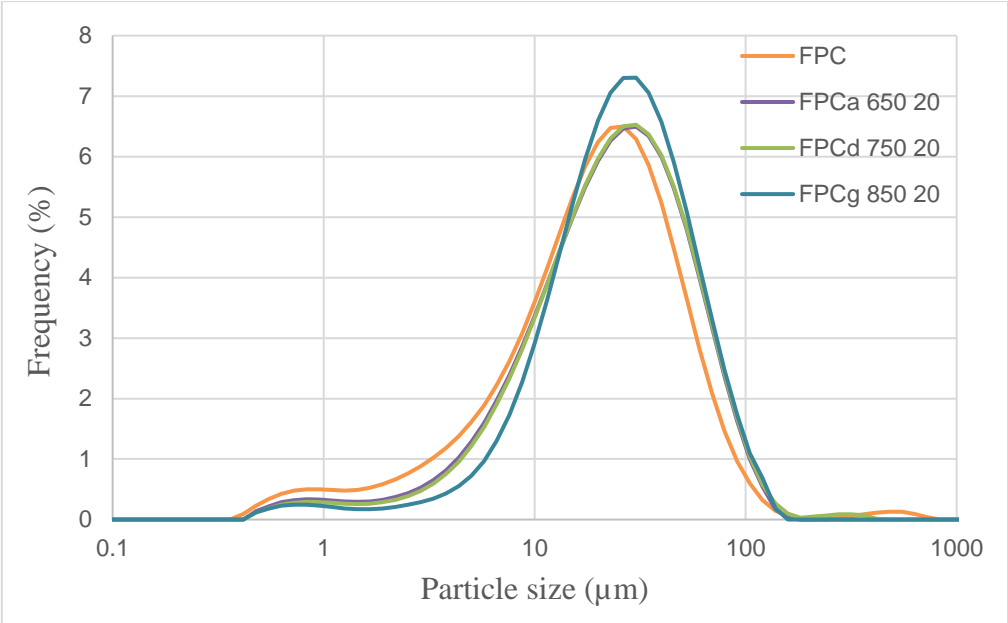


Figure 4.16 Particle size for 20 min FPC.
(from Laszlo Csetenyi)

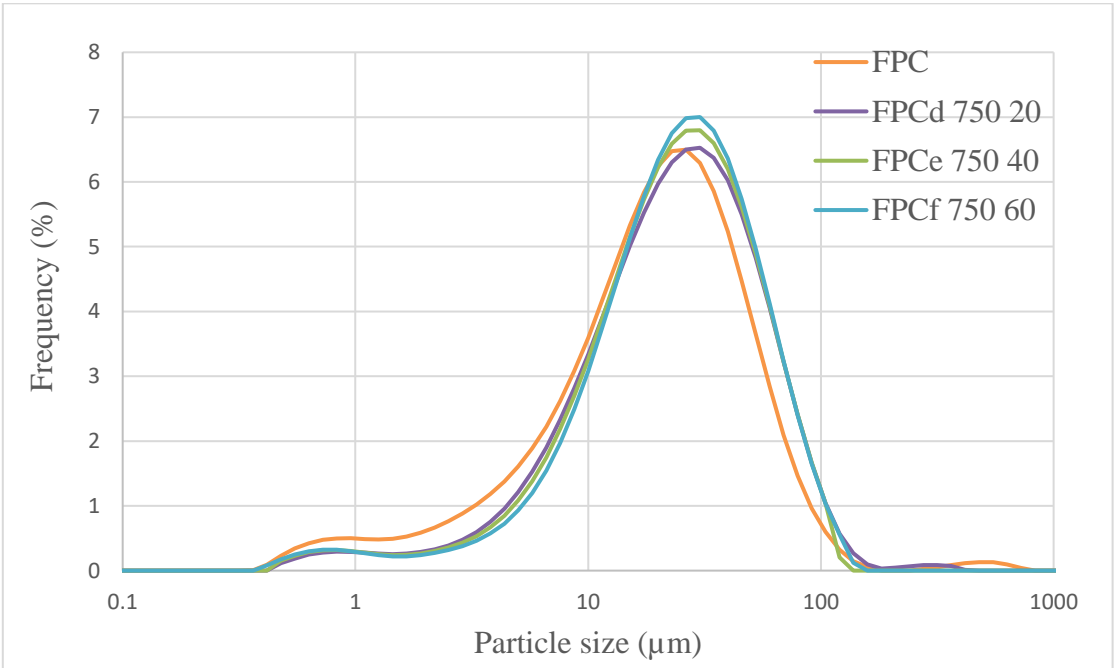


Figure 4.17 Particle size for 750°C FPC.
(from Laszlo Csetenyi)

4.2.4 BET

The specific surface area of the FPC samples was also determined using the BET method, which provides a more accurate measure of surface area by considering the physical adsorption of gas molecules. The BET results demonstrate a significant effect of heat treatment on SSA.

Table 4.7 SSA of FPC samples with BET (m²/g).

<i>Raw: 14.928 m²/g</i>	650 °C	750 °C	850 °C
<i>20 min</i>	15.396	12.161	3.503
<i>40 min</i>	14.204	6.507	2.486
<i>60 min</i>	12.650	4.562	2.326

The results indicate a considerable effect of heat treatment on SSA. As a matter of fact, it significantly reduces the SSA of FPC. These values confirm the expected behaviour of the clay: increasing the calcination temperature leads to a more pronounced reduction in SSA. However, the rate of reduction becomes less abrupt at higher temperatures, particularly beyond 750°C. The SSA values for samples calcined at 750°C show a dramatic decrease, especially after 20 minutes, which suggests substantial structural changes in the clay.

Nevertheless, the extent of change with longer residence time is definitely smaller, with only minor reduction in SSA observed. We can note that these findings are in line with those obtained previously with the LD experiment.

In conclusion, considering the minimal differences observed between 40 and 60 minutes of calcination, it is unnecessary to extend the process to one hour to achieve a relevant SSA and sufficient amorphous transformations, which are critical for optimal reactivity. The additional energy consumption and CO₂ emissions may not be justified.

Therefore, a calcination process at 750°C for 40 minutes appears to be the most favorable option. This temperature and duration yield one of the best proportions of quartz (23.34%) and amorphous content (64.24%) among all the samples tested.

4.2.5 General observations

Several challenges and observations were noted during the experiments:

XRD analysis :

The XRD results were somewhat inconsistent and difficult to interpret. Different analyses have been done, but each provides different outcomes. This issue had already been observed while our results for CC2F and CC9F were rather different than those providing in the previous study conducted at the University of Dundee. Therefore, we must be cautious about XRD results.

Activating solution :

We faced some difficulties preparing an optimal solution for the FPC clay. Indeed, although we tried the same various ratios as for CC2F and CC9F, the paste was not ideal. This could be due to the lack of accuracy of the XRD results, or also the presence of iron in the clay that may have influenced the reactivity. This demonstrates the importance of having a precise composition analysis to determine the correct ratio to activate the clay.



Figure 4.18 FPC test-samples with different ratios.

Moreover, this clay also has a high water demand, since the minimum w/c ratio required to obtain a workable paste was 0.55.

Calcination process:

The color differences highlight the need for a more controlled and uniform calcination process, such as using a tray or rotary kiln, to ensure consistent heating to avoid partial calcination, and thus variability in the results.



Figure 4.19 FPC samples after a 750°C calcination.

On a positive note, it's beneficial that the clay does not require an hour of calcination at 850°C, which helps in reducing both energy consumption and CO₂ emissions. This finding supports the earlier conclusion that a shorter calcination time at 750°C for 40 minutes is sufficient for achieving the desired material properties.

Moreover, iron in clay typically exists as iron oxides, such as Fe₂O₃ and Fe₃O₄. These oxides can influence the calcination temperature since they can lower the temperature at which certain mineral phases in the clay decompose or transform, such as quartz. This can potentially reduce the overall energy required for calcination.

Clay structure:

A hypothesis has been proposed regarding the clay's microstructure. During the calcination process, several changes occur, one of which may be the transformation of other phases, likely amorphous, into illite. This suggests that recrystallization is taking place during calcination. Such a reorganization into a more stable crystalline form like illite could contribute to the observed decrease in SSA.

5. Overall conclusions and recommendations

5.1 Overall conclusions and summary observations

This project investigated the potential use of waste clay for producing alkali-activated calcined clay as a sustainable alternative to ordinary Portland cement in the construction industry. The study involved characterising two calcined clays and one raw clay to identify the optimal alkali-activating solution. Analytical techniques were employed to assess chemical and mineralogical compositions and determine the most effective activation parameters.

The key findings from the study include:

- Necessary material properties:
Chemical and mineralogical analyses are crucial for tailoring activation solutions to each clay type due to significant variability in results. Accurate composition data ensure the development of effective activation ratios.
- Strength parameters:
The traditional w/c ratio is not applicable for calcined clay, as it varies widely with clay type. Instead, the Si/Al ratio better reflects the material's reactivity and resultant strength.
- Major role of iron:
Iron significantly impacts clay reactivity. For example, with iron accounted for, CC9F samples ceased to exhibit abnormal breakage patterns, improved in density (potentially reducing carbonation), and achieved setting times within the industry-recommended 4-8 hours.
- Optimal Calcination Parameters:
Calcination at 750°C for 40 minutes was found to optimise both reactivity and material performance. To avoid incomplete phase transformation, calcination should be conducted on a tray or in a rotary kiln, potentially reducing energy consumption.
- Low-iron clays suitability:
CC2F, which is low in iron content, demonstrated excellent performance, being easy to activate and practical for use.

In summary, alkali-activated calcined clays show promise as a viable alternative to traditional cement. The ongoing interest in sustainable practices, as evidenced by projects like the *Grand Paris Express*, suggests that the development of these materials could advance promptly. The variability in clay composition within the same region is manageable, making this technology increasingly feasible.

5.2 Recommendations for further research work

Considering these findings, future research should address the following areas:

- Iron role:
Further investigation is needed to define iron's role in the activation process to ensure optimal performance across various clay types, including those like CC9F.
- Cooling cycle:
The cooling phase is as important as the heating, affecting the fixation of amorphous phases and preventing unwanted recrystallization. Research should explore how different cooling strategies impact material properties.
- Activating ratios:
Further research should explore a wider range of ratios, especially on waste clays, to refine the findings and provide more accurate results.
- Durability tests:
Long-term durability and compressive strength of concrete and mortars produced from alkali-activated calcined clays need further evaluation to validate performance over time.
- Environmental impacts:
A thorough assessment of the environmental impacts of various cement and concrete production processes is essential to quantify the sustainability benefits of these materials.

Appendices

Appendix 1: The 37 types of common cements.

Main types	Notation of the 37 products (types of common cement)		Composition (percentage by mass ^a)											Minor additional constituents	
			Main constituents									Limestone			
			Clinker	Blast-furnace slag	Silica fume	Pozzolana		Fly ash		Burnt shale					
						natural	natural calcined	siliceous	calcareous						
Type name	Type notation	K	S	D ^b	P	Q	V	W	T	L	LL				
CEM I	Portland cement	CEM I	95-100	–	–	–	–	–	–	–	–	–	0-5		
	Portland-slag cement	CEM I/A-S	80-94	6-20	–	–	–	–	–	–	–	–	0-5		
		CEM I/B-S	65-79	21-35	–	–	–	–	–	–	–	–	0-5		
	Portland-silica fume cement	CEM I/A-D	90-94	–	6-10	–	–	–	–	–	–	–	0-5		
	Portland-pozzolana cement	CEM I/A-P	80-94	–	–	6-20	–	–	–	–	–	–	0-5		
		CEM I/B-P	65-79	–	–	21-35	–	–	–	–	–	–	0-5		
		CEM I/A-Q	80-94	–	–	–	6-20	–	–	–	–	–	0-5		
		CEM I/B-Q	65-79	–	–	–	21-35	–	–	–	–	–	0-5		
	Portland-fly ash cement	CEM I/A-V	80-94	–	–	–	–	6-20	–	–	–	–	0-5		
		CEM I/B-V	65-79	–	–	–	–	21-35	–	–	–	–	0-5		
		CEM I/A-W	80-94	–	–	–	–	–	6-20	–	–	–	0-5		
	CEM II	Portland-burnt shale cement	CEM I/A-T	80-94	–	–	–	–	–	–	6-20	–	–	0-5	
			CEM I/B-T	65-79	–	–	–	–	–	–	21-35	–	–	0-5	
			CEM I/A-L	80-94	–	–	–	–	–	–	–	6-20	–	0-5	
Portland-limestone cement		CEM I/B-L	65-79	–	–	–	–	–	–	–	21-35	–	0-5		
		CEM I/A-LL	80-94	–	–	–	–	–	–	–	–	6-20	0-5		
		CEM I/B-LL	65-79	–	–	–	–	–	–	–	–	21-35	0-5		
Portland-composite cement ^c		CEM I/A-M	80-88	12-20									0-5		
		CEM I/B-M	65-79	21-35									0-5		
		CEM I/C-M (S-L)	50-64	16-44	–	–	–	–	–	–	–	6-20	–	0-5	
		CEM I/C-M (S-LL)	50-64	16-44	–	–	–	–	–	–	–	6-20	–	0-5	
	CEM I/C-M (P-L)	50-64	–	–	16-44	–	–	–	–	–	6-20	–	0-5		
	CEM I/C-M (P-LL)	50-64	–	–	16-44	–	–	–	–	–	6-20	–	0-5		
	CEM I/C-M (V-L)	50-64	–	–	–	–	–	16-44	–	–	6-20	–	0-5		
CEM I/C-M (V-LL)	50-64	–	–	–	–	–	16-44	–	–	6-20	–	0-5			
CEM III	Blast furnace cement	CEM III/A	35-64	36-65	–	–	–	–	–	–	–	–	0-5		
		CEM III/B	20-34	66-80	–	–	–	–	–	–	–	–	0-5		
		CEM III/C	5-19	81-95	–	–	–	–	–	–	–	–	0-5		
CEM IV	Pozzolanic cement ^c	CEM IV/A	65-89	–	11-35				–	–	–	–	0-5		
		CEM IV/B	45-64	–	36-55				–	–	–	–	0-5		
CEM V	Slag-pozzolanic cement ^c	CEM V/A	40-64	18-30	–	18-30			–	–	–	–	0-5		
		CEM V/B	20-38	31-49	–	31-49			–	–	–	–	0-5		
CEM VI	Composite cement ^c	CEM VI (S-L)	35-49	31-59	–	–	–	–	–	–	6-20	–	0-5		
		CEM VI (S-LL)	35-49	31-59	–	–	–	–	–	–	–	6-20	0-5		
		CEM VI (S-V)	35-49	31-59	–	–	–	6-20	–	–	–	–	0-5		

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

^b The proportion of silica fume is limited to 10 %.

^c In Portland-composite cements CEM I/A-M, CEM I/B-M and CEM I/C-M, in Pozzolanic cements CEM IV/A and CEM IV/B, in Slag-pozzolanic cements CEM V/A and CEM V/B and in Composite cements CEM VI the main constituents other than clinker shall be declared by designation of the cement (for examples, see Clause 8).

Appendix 2 : The complete XRF data for CC2F and CC9F.

Sample	CC2F	CC9F
Element	Proportion (wt%)	Proportion (wt%)
<i>SiO₂</i>	53.779	60.065
<i>Al₂O₃</i>	34.651	22.934
<i>Fe₂O₃</i>	2.198	8.748
<i>K₂O</i>	4.584	1.213
<i>MgO</i>	0.372	0.993
<i>F</i>	0.226	-
<i>Na₂O</i>	0.189	0.157
<i>CaO</i>	0.161	2.353
<i>TiO₂</i>	0.153	1.261
<i>SO₃</i>	-	0.128
<i>Cu</i>	< 0.1	< 0.1
<i>P₂O₅</i>	< 0.1	< 0.1
<i>Cr</i>	< 0.1	< 0.1
<i>Pb</i>	< 0.1	-
<i>Zn</i>	< 0.1	< 0.1
<i>Ga</i>	< 0.1	< 0.1
<i>As</i>	< 0.1	< 0.1
<i>Rb</i>	< 0.1	< 0.1
<i>Y</i>	< 0.1	< 0.1
<i>Zr</i>	< 0.1	< 0.1
<i>Nb</i>	< 0.1	< 0.1
<i>Sn</i>	< 0.1	-
<i>Ba</i>	< 0.1	< 0.1
<i>Tl</i>	< 0.1	-
<i>MnO</i>	< 0.1	< 0.1
<i>Cm</i>	-	< 0.1
<i>Sr</i>	-	< 0.1
<i>Ce</i>	-	< 0.1
<i>Ni</i>	-	< 0.1
<i>Cl</i>	-	< 0.1
Total	96.313	97.852

Appendix 3: Oxide composition of various clay brick powder.

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Table 1
Oxide composition of CBP (%).

Reference	Oxide composition						
	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O
Chen et al. (2011)	68.10	16.35	2.05	6.04	1.43	1.20	2.38
Cheng et al. (2022)	62.27	14.27	6.79	6.22	2.24	1.48	2.67
Duan et al. (2020)	64.11	18.77	2.49	7.35	1.93	1.64	2.53
György et al. (2019)	64.46	16.94	3.23	6.13	2.59	2.16	1.89
Hwang et al. (2019a)	61.25	17.00	11.34	1.67	1.62	2.04	3.30
Li et al. (2016)	67.95	17.25	1.35	6.93	1.52	1.31	2.33
Li et al. (2019)	60.56	17.16	10.7	3.46	1.78	1.26	2.50
Likes et al. (2022)	69.87	20.98	0.40	3.61	0.39	0.59	2.42
Liu et al. (2021)	66.54	14.88	4.24	6.62	2.73	1.03	1.42
Ma et al. (2023)	52.37	12.5	22.83	2.41	1.44	0.24	2.46
Martin et al. (2018)	55.50	17.10	10.50	5.80	4.50	1.90	2.80
Naceri and Hamina (2009)	66.52	14.2	6.06	5.45	2.35	0.67	2.09
Olofinnade1 et al. (2016)	60.64	14.23	0.27	4.93	1.72	1.94	1.44
Ouyang et al. (2021)	65.70	19.45	1.45	7.98	0.94	0.45	2.44
Ozcelikci et al. (2023)	52.4	19.9	4.18	7.92	2.84	1.58	3.72
Rovnanfk et al. (2016)	57.67	14.91	9.81	5.02	3.74	1.45	3.20
Si-Ahmed and Kenai (2020)	58.41	9.72	15.81	5.47	2.13	0.12	1.75
Wu et al. (2011)	68.10	16.35	2.05	6.04	1.43	1.20	2.38
Wu et al. (2021a)	66.81	17.62	1.82	7.68	1.36	1.04	2.43
Zhao et al. (2020)	64.50	18.40	1.90	8.00	1.50	1.10	2.70
AVG	62.69	16.40	5.96	5.74	2.01	1.22	2.44

(Wu and Gao, 2024)

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