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Clay-based geopolymer as the sole binder in concrete

Master's thesis in Civil and Environmental Engineering
Supervisor: Prof. Roar Myrdal
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Master`s thesis

NTNU
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SUMMARY:

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This study investigates the viability and suitability of local marine clay and pottery white clay as the sole binder and complete replacement for cement in concrete. The clays were calcined at temperatures of (600°C, 700°C, and 850°C), and then proportioned and casted with the addition of alkaline activators NaOH (45%), Na_2SiO_3 (35%) and Ca $(OH)_2$. The mortar specimens were cured in two different temperatures and subsequently subjected to several testes. Mechanical tests, including flexural and compressive strength were conducted to evaluate the clay materials performance compared to the specimens made of standard cement(reference), as well as to each other after 7 and 28 days of curing. Additionally, the thermal resistance of the clay specimens was tested by subjecting them to propane flame and their acid resistance was assessed and compared to reference specimens by submerging the specimens into HCl 10% for 48hour.

The results of the mechanical tests show that the clay specimens, at all three calcination temperatures, exhibit significantly low flexural and compressive strength compared to the specimens made of standard cement (reference), which suggest that the clay materials might not possess the desired strength properties to serve as the complete replacement of OPC. However, the thermal and acid resistance tests show that clay-based materials obtain an exceptional fire resistance and a superior resistance to acidic environments compared to the standard cement.

RESPONSIBLE TEACHER: Prof. Roar Myrdal

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Department of Structural Engineering
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MASTER'S THESIS IN CIVIL AND ENVIRONMENTAL ENGINEERING

2023

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Abstract

The decreasing availability of geopolymers such Fly Ash (FA) and Ground Granulated Blast Furnace Slag (GGBS), along with growing demand for supplementary materials to replace Ordinary Portland Cement (OPC) in concrete industry, highlights the need for an eco-friendly and easily accessible alternative replacement. Whit the limited supply of FA and GGBS, the abundant availability of local calcined clay offers a promising and sustainable solution for the replacing of OPC. However, the effectiveness of calcined clay as cement replacement is influenced by various factors such as the amount and type of clay, its mineralogy, and the calcination temperature.

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Sammendrag

Den minskende tilgjengeligheten av geopolymere slik som flygeaske (FA) og Slagg (GGBS), i kombinasjon med en økende etterspørsel etter supplementære materialer for å erstatte Portlandsement (OPC) i betongindustrien, understreker behovet for et miljøvennlig og lett tilgjengelig alternative erstatning. Med den begrensede tilførselen av FA og GGBS, tilbyr den rikelige tilgjengeligheten av lokal kalsinert leire et lovende og bærekraftig alternativ for erstatning av OPC. Effektiviteten av kalsinert leire som sementerstatning er derimot påvirket av forskjellige faktorer som mengden og leiretype, dens mineralogi, og kalsineringstemperaturen.

Denne studien undersøker muligheten og egenheten av lokal marin leire og keramisk hvit leire som eneste bindemiddel og fullstendig erstatning for sement i betong. Leirene ble kalsinert ved temperaturer på (600°C, 700°C og 850°C), og deretter dosert og støpt med tilsetning av alkaliske aktivatorer NaOH (45%), Na_2SiO_3(35%) and $Ca(OH)_2$. Mørtelprøvene ble herdet ved to ulike temperaturer og ble deretter utsatt for en rekke tester. Bøyefasthet- og trykkfasthetstester ble utført for å evaluere leirematerialenes egenskaper og ytelse sammenliknet med referanseprøver laget av standard sement, samt for å sammenligne ytelsen til de ulike leireprøvene med hverandre etter 7 og 28 dagers herding. I tillegg ble den brannmotstanden til leireprøvene testet ved å utsette dem for propanflamme, og deres syremotstand ble vurdert og sammenliknet med referanseprøvene ved å nedsenke prøvene i HCl 10% i 48 timer.

Resultatene fra bøyefasthet- og trykkfasthetstestene vise at leireprøvene ved alle tre kalsineringstemperaturer har betydelig lavere styrke sammenlignet med sementprøvene(referanse). Dette antyder at leirematerialene kanskje ikke har de nødvendige styrkeegenskapene som kreves for å fungere som fullstendig erstatning for OPC. Imidlertid viser brannmotstand- og syremotstandstestene at leireprøvene har en enestående motstand mot brann og en overlegen motstand mot sure miljøer sammenlignet med sementprøvene.

Preface

This master's thesis was written during the spring of 2023 at the Norwegian University of Science and Technology. This thesis is the final work of my 5 years master's engineering program at the Department of Structural Engineering at NTNU Trondheim.

First and foremost, I would like to extend my sincere gratitude to my supervisor, Prof. Roar Myrdal, for his invaluable guidance and unwavering support throughout the entire duration of this study. His expertise and insightful feedback have been invaluable in guiding me throughout this project.

I would also like to express my appreciation to the staff at the concrete laboratory at the Department of Structural Engineering, SINTEF, and the Geotechnics group of the Department of Civil and Environmental Engineering at NTNU. Their assistance and cooperation were indispensable in conducting the experiments and gathering the necessary data for this study.

Finally, I would like to express my deepest gratitude to my friends for their unwavering support, encouragement throughout this project and for the great 5 years that we have had together.

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1. Introduction

Geopolymers are inorganic polymers made by the reaction between amorphous aluminosilicate like Fly Ash (FA), Calcined-Clay, Ground Granulated Blast Furnace Slag (GGBS), and/or Silica Fume, and an alkaline activator solution typically consisting of alkali hydroxide and sodium silicate. Since their development by *J. Davidovits* in the late 1970s and early 1980s, they have become increasingly prominent within the construction industry (1). Geopolymers are suitable eco-friendly alternatives to Ordinary Portland Cement (OPC), which is responsible for approximately 8% of CO_2 emissions (2). They have lower energy consumption compared to OPC, thereby reducing CO_2 emissions in concrete production (3,4). Geopolymers offer additional benefits such as high heat resistance, high acid tolerance, and less shrinkage, which contribute to their remarkable durability (1,5,6).

However, the availability of geopolymers like Fly Ash (FA) and Ground Granulated Blast Furnace Slag (GGBS) in Europe and the US is decreasing due to the decommissioning of coal-fired power plants as a result of transitioning to greener and renewable energy sources (7–9). On the other hand, the availability of Calcined-Clay is unlimited as it is shown in *figure 1*, especially local clay that is easy to access(10).
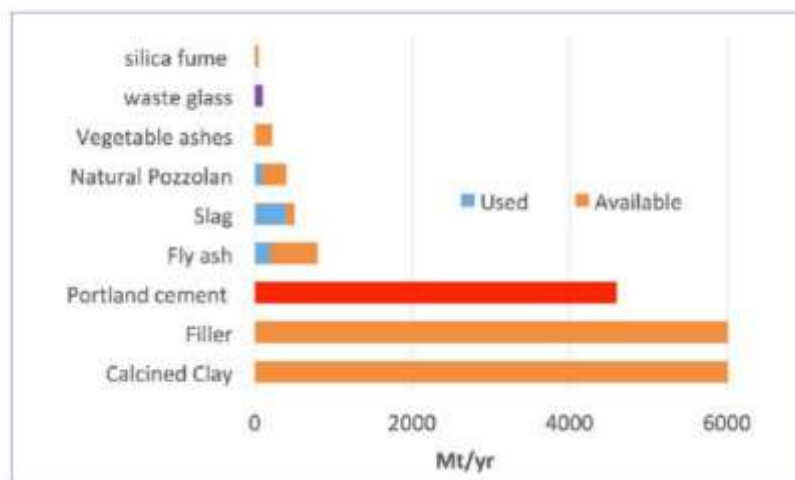
Figure 1. The utilization and estimated availability of potential supplementary cementitious materials (SCMs) and fillers depend on logistical, precise chemical and mineralogical composition, potential contamination, and the local availability of other raw materials. Source (10)

Although the use of calcined clay as a pozzolanic additive/substitute for cement in concrete is not new and has been studied in the past decades, it has typically been with the clinker content of 65-70 % (11). However, research on the utilization of local marine clay in Norway as a geopolymer binder, serving as the sole and100% substitute for cement, has been limited. The need for further studies on local marine clay has become more apparent when considering the difference between marine clay in Norway and the clay in the rest of the world, which was not covered under the ice during the last ice age.

1.1 Clay

In this study, two different types of clay, namely local marine clay, and pottery white clay were selected for investigation. The local marine clay used in this study was sourced from the Tiller-Flotten test field, and it is a type of quick clay that is commonly studied and tested in the geotechnical laboratory at NTNU shown in *figure 2*. This material has a significant clay content of approximately 68% (fraction <2 μm). The clay composition consists of various minerals, with 26% biotite, 23% illite/muscovite, 16% chlorite, 13%

plagioclase, 7% amphibole, 7% quartz, and 4-6% potassium feldspar being the major components (12). The other clay used in this study is a pottery white clay known as K148 shown in figure 3, supplied by Sibelco and originating from Germany. It was obtained in a 10 kg package for use in the experimental investigations (13).

Figure 2. The local marine clay from Tiller-Flotten.

Figure 3. The pottery white clay from Germany.

1.2 Cement

Portland cement is the primary binder in concrete, making it indispensable component in concrete. Developed by Joseph Aspin and patented in 1824, Portland cement revolutionized the construction industry with its remarkable properties, such as remarkable ability to form a strong and durable bond between aggregates, resulting in creation of solid and robust concrete structures(14). The main constituent (90-95%) in Ordinary Portland Cement (OPC) is limestone ($CaCO_3$), which is mixed with minor constituents (5-10%) that provide additional elements such as Fe_2O_3, SiO_2, Al_2O_3, and others. The calcination process of Portland clinker occurs when it is heated up to 1450°C, resulting in the conversion of $CaCO_3$ into CaO and CO_2. This process produces approximately 0.9 tonne of CO2 per tonne of cement. Portland cement has 4 major phase and 4 oxide phase as shown in *figure 4* (14).

Major Phases	Mineralogical term	Shortened cement chemical notation	Cement chemical notation (Oxide notation)
Tricalcium silicate	Alite	C_3S	$3CaO . SiO_2$
Dicalcium silicate	Belite	C_2S	$2CaO . SiO_2$
Tricalcium aluminate	Aluminate	C_3A	$3CaO . Al_2O_3$
Tetracalcium aluminoferrate	Ferrite	C_4AF	$4CaO . Al_2O_3 . Fe_2O_3$

Figure 4. The four major phase and the four-oxide phase of the Ordinary Portland Cement (OPC) clinker. Source (14).

The cement used in this study is CEM II shown in *figure 5*, which is the standard cement FA produced by *Norcem* and it is their main product. It is designed to suit the conditions in Norway. It can be used alongside alkali-reactive aggregates and is applicable in various exposure, strength, and durability classes(15).

Figure 5. The standard cement FA (CME ll) form Norcem used in this project.

1.3 Aggregates

Aggregates in concrete, which includes sand and rock materials, are essential components in concrete. The size, shape and mineralogy of the aggregates have significant effects on the properties of concrete, both in fresh and hardened state (14). In the fresh state, aggregates can influence the workability (ease of placing and working), water demand (amount water needed for proper hydration and workability) and stability (ability to maintain homogeneity and prevent segregation) of the fresh concrete (14). In the

hardened state, aggregations can influence the strength (compressive, tensile, and flexural), density (porosity and weight), thermal properties (thermal conductivity and expansion) and durability (resistance to weathering, abrasion, and chemical attacks) of the concrete. These factors emphasize the importance of selecting appropriate aggregates and ensuring their proper grading, quality, and compatibility with the cement paste for achieving desired concrete performance. Aggregates are divided into fine aggregate (0-8mm), referred to as sand, and coarse aggregates larger than 8mm. Sand (0-2mm), which is used in this project shown in *figure 6*, plays a crucial role in mortar as its strongest and most rigid component. It occupies a significant proportion, approximately 65% to 75% of the concrete volume, and it is critical to ensure it has the appropriate grain size (14).

Figure 6. The standard mortar sand (0-2mm) used in this project.

1.4 Admixture and chemicals

Admixtures are group of chemicals or mineral additives that are added into concrete during the mixing process to alter properties of the mix in fresh and/or hardened state(14). Although additives are typically added in small quantities less than 5% by the masse of cement and EN 934-2 standard classifies them into 11 classes with 5 most used are shown in *figure 7*. Superplasticizers are high-range water reducers, which improve workability and flowability if the mix, by dispersing and separating the cement/clay particles, allowing them to move freely, which reduces friction between them. *Dynamon SR-N* is the superplasticizer used in this project, which is liquid additive from Mapeis DDP-technology (16). As a superplasticizer it helped to reduce the amount water, which helped to have a water-binder ratio(w/b) of 0.5. The decision to use *Dynamon SR-N* as superplasticizer in the project was solely based on its availability in the lab.

Main classes	Definition / mode of action
Plasticiser / water reducer	Admixture which, without effecting the consistence, permits a reduction in the water content of a given concrete mix, or which, without affecting the water content increases the slump/flow or produces both effects simultaneously.
Superplasticiser	Admixture which, without effecting the consistence, permits a **high** reduction in the water content of a given concrete mix, or which, without affecting the water content increases the slump/flow **considerably** or produces both effects simultaneously.
Air entrainer	Admixture which allows a controlled quantity of small, uniformly distributed air bubbles to be incorporated during mixing which remain after hardening.
Set and hardening accelerators	Admixtures which accelerate the **set** by decreasing the time when the mix changes from the plastic to the rigid state and/or which accelerate the **hardening** by increasing the early strength gain.
Set retarder	Admixture which retards the set by increasing the time when the mix changes from the plastic to the rigid state.

Figure 7. The 5 most used additives in concrete. Source(14)

The process of geopolymerization involves the reaction of an aluminosilicate source, such as clay, with an alkaline activator solution as shown in *figure 8* (9,17). The role of alkaline activators is pivotal in initiating and regulating the geopolymerization reaction. Alkaline activators provide the necessary alkalinity to activate the clay minerals and facilitate the formation of polymeric structures. Alkaline activators used in clay-based geopolymers typically consist of a combination of alkaline materials, such as sodium hydroxide (NaOH), potassium hydroxide (KOH), and/or sodium silicate (Na_2SiO_3)(18). The interaction between alkaline activators and source materials is a complex chemical process that involves hydrolysis, polycondensation, and polymerization reactions. Alkaline activators dissociate into hydroxyl ions (OH-) upon contact with water, which then react with the silicates present in the source materials to form a gel-like precursor. This precursor subsequently undergoes condensation reactions, leading to the formation of a hardened geopolymer structure. The alkali concentration, ratio of activator to source materials, and curing conditions significantly influence the final properties of the geopolymer product (18).
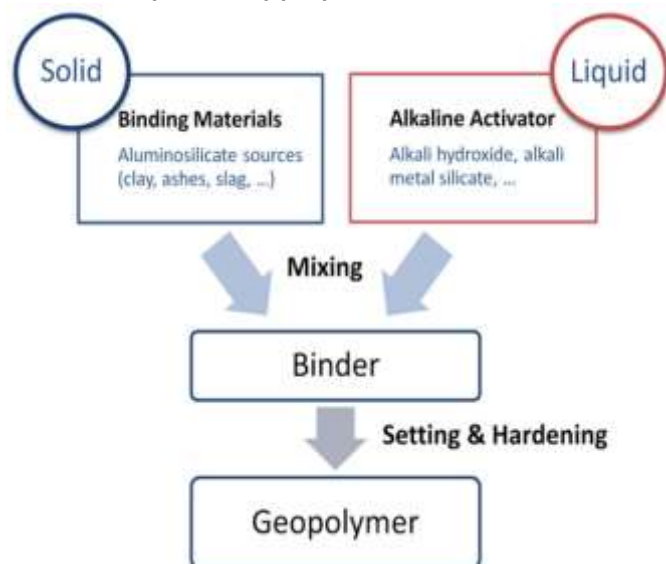
Figure 8. The schematic diagram of geopolymer formation. Source(17)

In this study sodium silicate (Na_2SiO_3) with a concentration of 35% alongside sodium hydroxide (NaOH) with concentration of 45% and calcium hydroxide ($Ca(OH)_2$) have been used. NaOH at 45% concentration and Na_2SiO_3 at 35% concentration aid in dissolving the silicon (Si) and aluminum (Al) oxides present in the source materials, allowing them to react and contribute to geopolymer gel formation. High concentrations of NaOH may accelerate the reaction kinetics, leading to faster setting times. However, it's essential to carefully control the concentration to prevent excessive acceleration, which can affect workability and result in reduced strength. Silica in sodium silicate participates in the polymerization process, forming the Si-O-Si bonds that contribute to the three-dimensional network structure of the geopolymer. High concentrations of sodium silicate such as 35% can increase the alkalinity and reactive silica content, promoting the geopolymerization reactions. However, it's important to note that the specific concentration and formulation of the geopolymer mix may vary depending on the clay type, desired properties, and specific application requirement.

1.5 Objectives

The purpose of this study is to assess the suitability of local marine clay and pottery white clay as the sole binder, and complete replacement for Ordinary Portland cement (OPC), as well as other geopolymers like Fly Ash (FA) and Ground Granulated Blast Furnace Slag (GGBS), in concrete. To achieve this objective, a series of experimental methods were implemented. Two types of clay, namely local marine clay from Tiller-Flotten and pottery white clay from Germany, were dried, grinded, sifted and calcined at three different temperatures (600°C, 700°C, and 850°C). The resulting calcined clays with addition of alkaline activators NaOH (45%), Na_2SiO_3 (35%) and Ca $(OH)_2$, were then proportioned and used to cast mortar specimens, which were cured using two different methods: one set was cured in a heating cabinet at 60°C for (22 ±2) hours before moving it to the curing room, while the other set was cured directly in the curing room. Following the curing process, the samples underwent various tests to evaluate their performance in comparison to the reference specimens made of standard cement and to each other. The conducted tests included:

-   Flexural strength test after 7 and 28 days of curing
-   Compressive strength test after 7 and 28 days of curing
-   Fire and thermal resistance test
-   Acid resistance test

2. Methodology

2.1 Drying, grinding, and sifting

The marine clay used in this study is from Tiller-Flotten NGI's test site, and the pottery white clay (K148 by Sibelco) from Germany. The clays were obtained from the geotechnical laboratory at NTNU (Norwegian University of Science and Technology). To facilitate the drying process more effectively, the clays were sliced into smaller pieces. They were then dried in a heating/drying cabinet at a temperature of 105°C for 36 hours as shown in *figure 9*. It was noticed that this initial drying process was not sufficient to completely dry the clays, so they were manually ground into smaller pieces before being dried in the cabinet for an additional 36 hours at the same temperature as it is shown in *figure 10*. The complete drying of the clays was important to make the subsequent grinding and sifting processes easier. Insufficient drying could have made these processes more challenging or less effective.

Figure 9. A. shows the local marine clay sliced into pieces and B. shows the clay materials were dried in the drying cabinet at 105°C for 36 hours.

Figure 10. A. Manual grinding of clay to smaller pieces. B. Drying of manually grinded clay in the cabinet at 105°C for 36 more hours.

Furthermore, the clays were manually ground into even smaller pieces, and then a grinder from SINTEF (*see Appendix A1*) was used to further grind the clays into the powder as it can be seen in figure *11*. In the next step, the powdered clays were sifted using a sifting machine. The sifting machine has sieves with various sizes, ranging from 500µm down to 63µm. The powdered clays were sifted using the two smallest sieves with sizes ranging from 125µm down to 63µm as it is shown in *figure 12*, which is the smallest sieve size available. The initial goal was to sift the powdered clays through the 63µm sieve size, but it proved to be challenging. As a result, all the local marine clay used in the project was sifted through a 125µm sieve, and 55% of the clay passed through a 63µm sieve.

Figure 11. Shows the grinding process of the clay with the grinder from SINTEF.

This indicates that the local marine clay has a fineness of approximately (63µm<45%<125µm) and (55%<63µm). On the other hand, pottery white clay exhibits a fineness of approximately (63µm<43%<125µm) and (57%<63µm). Although it is safe to assume that local marine clay has a higher fineness below 63µm, in the range of less than 2µm, this assumption is based on the available data regarding its mineralogy which indicates the approximately 68% (fraction<2µm). Additionally, during the sifting process, it was observed that the clay exhibited high cohesiveness, which made it challenging to pass through the 63µm sieve. The lack of availability of more sophisticated instruments, such as a Blaine fineness meter, hindered the precise measurement of the fineness range of the calcined clays. This limitation made it challenging to obtain a more detailed assessment of the clay's fineness.
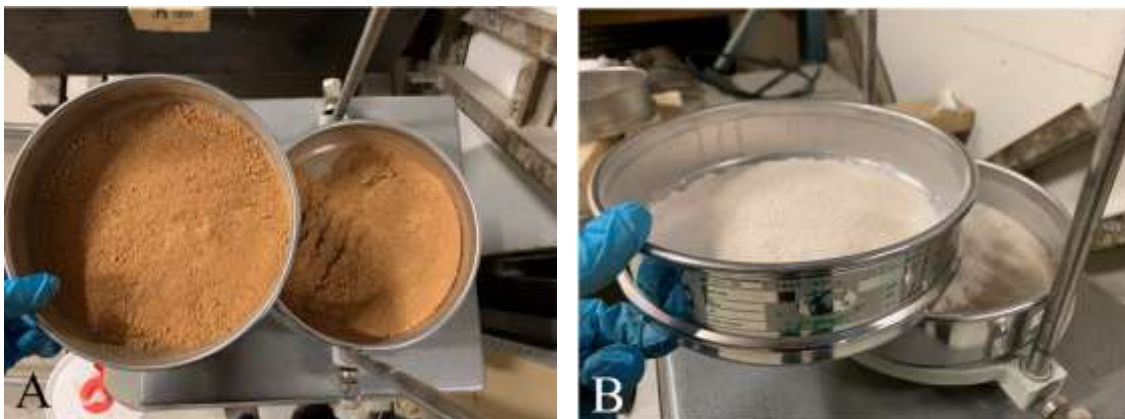

Figure 12. The sifting process using a sifting machine to range of 125µm down to 63µm. A. Shows sifting of local marine clay and B. shows sifting of pottery white clay.

2.2 Calcination process

Calcination is a process which involves heating the clay to high temperature, to remove chemically bound water, and removing hydroxyl group (OH) from the material, which will lead to change in the clay's chemical composition and structure (19). The calcination temperature is typically from 550°C to 1000°C, although the calcination temperature depends on the type of clay used (e.g., kaolin, illite etc.), the desired characteristic of the final product, and the specific geopolymer formulation (20–22). Several studies indicate that the optimal calcination temperature for kaolinite is around 700°C, as calcination below 700°C may result in less reactive metakaolinite, and reactivity also declines with calcination above 850°C (20,22). For illite clay, the optimal calcination temperature has been reported to be between 800°C and 950°C, which is higher than that of kaolinite (23,24).

The mineralogy of the local marine clay consists of approximately 26% biotite, 23% illite/muscovite, 16% chlorite, 13% plagioclase, 7% amphibole, 7% quartz, and 4-6% potassium feldspar, indicating a significant presence of biotite and illite (12). Based on this composition, it was decided to calcine the clay at three different temperatures: 600°C, 700°C, and 850°C. This decision was made to assess and compare the clay's performance at different temperatures and evaluate how varying temperatures affect the strength of the clay in the final tests. Additionally, due to the lack of information regarding the mineralogy of the pottery white clay and the desire to assess and compare its performance to the local marine clay, it was also decided to calcine it at the same different temperatures.

During the calcination process, the clays were poured into percaline bowls and heated to the desired temperatures using a Nabertherm oven at the SINTEF facility. The clays were maintained at 600°C, 700°C, and 850°C for 2 hours as shown in the *figure 13* and *figure 14*. Following the 2-hour duration, the temperature was lowered to 450°C without removing the bowls from the oven. Subsequently, the bowls were taken out of the oven and allowed to cool down to room temperature as it shown in *Appendix A2*.

Figure 13. Calcination process of local marine clay at 600°C, 700°C, and 850°C. A. shows the clay in the oven before calcination and B. shows the clay after the calcination.

While the literature emphasizes the significance of the temperature in the calcination process, it suggests that the importance of cooling, including cooling time and rate, is relatively minimal (25). During the calcination process, the local marine clay exhibited a weight loss of approximately 2.9% to 3.0% at all three temperatures, whereas the pottery white clay experienced a weight loss of 3.5% to 3.7%.
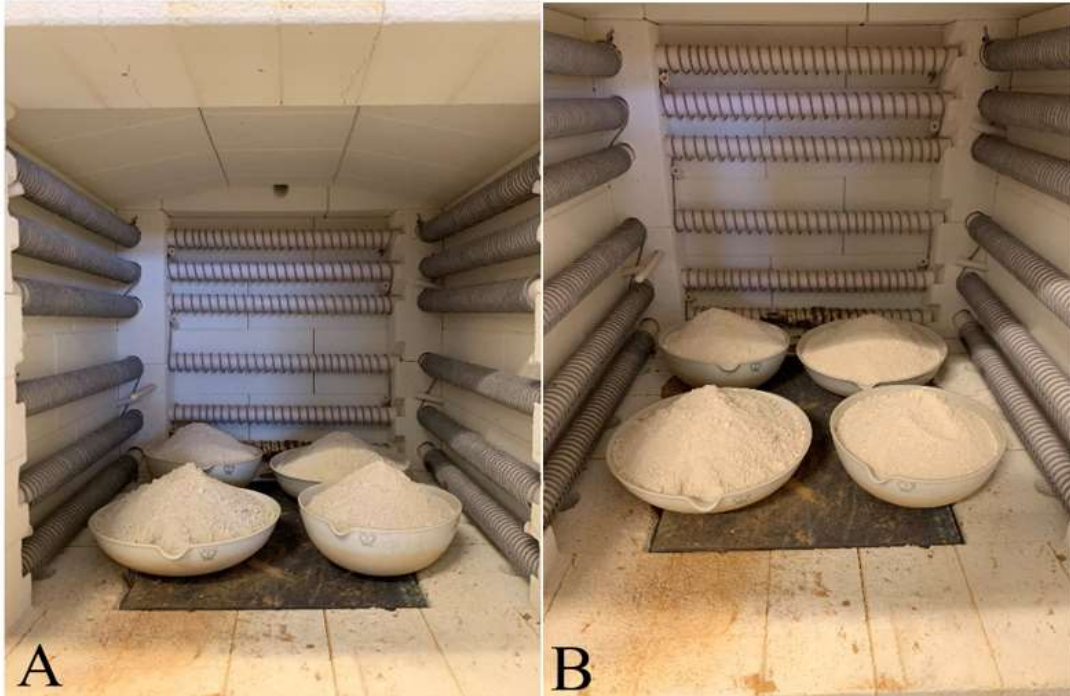

Figure 14. Calcination process of pottery white clay at 600°C, 700°C, and 850°C. A. shows the clay in the oven before calcination and B. shows the clay after the calcination.

2.3 Proportioning and mix design

Due to the uncertainties involved in concrete and mortar proportioning, conducting trial mixes is a common and valuable practice that aids in controlling and adjusting workability (14). After performing two trial mixes using local marine clay, it was concluded that a water-to-binder ratio (w/b) of 0.5 would be suitable. The decision to exclusively use local marine clay for the trial mixes was made due to the unavailability of cement in the lab at that particular time. Furthermore, we knew that the local marine clay has a high clay content, approximately 68%, with a fraction smaller than 2µm, indicating a large surface area (26). This characteristic implied a greater water demand for the clay.

Table *A* and Table *B* present the compositions of the mixes containing Portland cement, local marine clay, and pottery white clay. Table A represents the reference mix alongside the local marine clay at temperatures of 600°C, 700°C, and 850°C. On the other hand, Table B includes the mixes with the pottery white clay at the same temperatures alongside the reference mix. The reference mix contains Portland cement, standard mortar sand, water, and superplasticizer. In the mixes with clays, alkaline activator materials, such as sodium hydroxide (NaOH 45%) and sodium silicate (Na_2SiO_3 35%), were added in the amounts of 60g and 120g, respectively. The only distinction between Table A and Table B is the substitution of local marine clay with pottery white clay. The quantities mentioned in the tables represent the precise amounts of materials used in the mixes, with an accuracy of 1.0g.

Table A: Mixing chart for mixes with cement, and local marine clay at 600°C, 700°C and 850°C.

Type of material	Reference	Local marine clay		
Material	Cement	1	2	3
Sand(0-2mm) (g)	1200	1200	1200	1200
CEM II (g)	480	0	0	0
Clay (g)	0	411	411	411
Na_2SiO_3 (35%) (g)	0	120	120	120
NaOH (45%) (g)	0	60	60	60
Water (g)	240	129	129	129
Water-binder ratio (w/b)	0.50	0.50	0.50	0.50
Superplasticizer (SP) (g)	3	3	3	3
Calcination temperature (°C)	1300-1450	600	700	850

Table B: Mixing chart for mixes with cement, and pottery white clay at 600°C, 700°C and 850°C.

Type of material	Reference	Pottery white clay		
Material	Cement	1	2	3
Sand(0-2mm) (g)	1200	1200	1200	1200
CEM II (g)	480	0	0	0
Clay (g)	0	411	411	411
Na_2SiO_3 (35%) (g)	0	120	120	120
NaOH (45%) (g)	0	60	60	60
Water (g)	240	129	129	129
Water-binder ratio (w/b)	0.50	0.50	0.50	0.50
Superplasticizer (SP) (g)	3	3	3	3
Calcination temperature (°C)	1300-1450	600	700	850

In this study, two sets of specimens were proportioned and casted with replacing sodium hydroxide (NaOH 45%) with calcium hydroxide (Ca(OH)$_2$) to investigate the effect of calcium hydroxide on mechanical strength of the local marine clay. Table C illustrates the composition of mixes in which sodium hydroxide (NaOH 45%) from mixes 1 and 2 is replaced with calcium hydroxide (Ca(OH)$_2$). The dry portion of 60g of sodium hydroxide (NaOH 45%), equivalent to 27g, is divided and added to the amount of sodium silicate (Na$_2$SiO$_3$ 35%) and clay. Specifically, 8.4g out of the 27g of NaOH 45% is added to the quantity of Na$_2$SiO$_3$ 35%, increasing it from the previous 120g to 144g. the rest which is 18.6g out of the 27g is added to the clay, resulting in an increase from 411g to 429.6g.

In mix 1, which consists of local marine clay at 700°C, 11.5% of the clay is replaced with Ca(OH)$_2$. This substitution reduces the amount of clay from 429.5g to 380.2g, indicating that the quantity of Ca(OH)$_2$ used is 49.4g. In the mix 2, which consists of local marine clay at 850 °C, 10% of the clay is substituted by Ca(OH)$_2$. As a result, the amount of clay is decreased to 386.6, indicating that the amount of Ca(OH)$_2$ used is 43g.

Table C: Mixing chart for mixes with local marine clay with Ca (OH)$_2$

Type of material	Local marine clay	
Material	1	2
Sand(0-2mm) (g)	1200	1200
Clay (g)	380.2	386.6
Ca (OH)$_2$ (g)	49.4	43
Na$_2$SiO$_3$ (35%) (g)	144	144
Water (g)	297.7	366.7
Water-binder ratio (w/b)	0.82	0.96
Superplasticizer (SP) (g)	6	6
Calcination temperature (°C)	700	850

2.4 Mixing

The mixing equipment used for mortar mixing adhered to the specifications outlined in the NS-EN-196-1:2016 standard. A mixer with stemless steel bowl was used for the mixing as it can be seen in *figure 15*. Before the mixing, all the constituents were weighed with as much precision as possible. The alkaline activators, such as NaOH (45%) and Na$_2$SiO$_3$ (35%), were added to the water and stirred to ensure thorough and complete mixing. The mixing process was conducted following the instructions provided in the laboratory exercise for the Concrete Technology 1 course (14). It involved a sequence of steps: 1 minute of dry mixing for all the dry constituents, followed by 2 minutes of wet mixing after the addition of water and addition of superplasticizer (SP) while the mixing was ongoing. This was followed by a 2-minute rest period and concluded with 1 minute of final mixing figure *16*.

Figure 15. The mixer used during the mixing of mortar.

Figure 16. Shows the mixing of the materials. A. Local marine clay, B. Pottery white clay and C. standard cement (reference).

2.5 Casting

During the casting process, horizontal compartments with a cross-section of 40mm x 40mm and a length of 160mm were utilized as moulds. These dimensions conform to the specifications outlined in the NS-EN-196-1:2016 standard, which is a dedicated standard for testing mortars. The casting process was carried out as follows: First, the moulds were sprayed with form oil to facilitate the easy release of the specimens during the demoulding process and enhance the durability of the moulds. Then, the moulds were filled approximately halfway with mortar and compacted using a trowel. A shovel was utilized to ensure that the mortar reached the walls and corners of the moulds, eliminating any potential air pockets as it can be seen in *Figure 17*. After that, the moulds were completely filled with the mortar, and the compacting and air pocket eliminating process was repeated as it is shown in *figure 17.*

A vibrating table was utilized during the casting process to achieve better compaction, aligning with the equipment and procedures specified in the NS-EN-196-1:2016 standard. The surface of the mortar was leveled, excess material was removed, and finally, the moulds were placed in plastic bags to ensure the preservation of moisture content. Four sets of each test specimen were cast. Two of these sets were intended for 7-day testing, where one set was placed in a plastic bag and directly placed in the curing room, while the other set was placed in a plastic bag and placed in a heating cabinet at 60°C for (22±2) hours before being moved to the curing room. The same procedure was followed for the two sets of 28-day specimens. However, the reference test specimens, which contain only cement, and the test specimens which contain calcium hydroxide $(Ca(OH)_2)$ were placed only in the curing room and not in the heating cabinet. In total 30 sets of test specimens were cast.

Figure 17. Casting process: The moulds were filed halfway, compacted with trowel and shovel, then the moulds were completely field with mortar and the compacting procedure was repeated. A vibrating table was used during casting.

2.6 Curing

Curing of the test specimens was done in the curing room at a temperature of (20 ±1) °C and a relative humidity (RH) of (70 ± 2) % (*See Appendix A3*), in accordance with the requirements outlined in the NS-EN-196-1:2016 standard. The specimens were demoulded after (24±4) hours, meeting the requirements of both the NS-EN-196-1:2016 and NS-EN 12390-2:2019 standards. After demoulding, the specimens were placed inside the plastic bags, and stored horizontally in the curing room. As mentioned earlier (in the casting process section), with the exception of the reference specimens and the specimens with local marine clay calcined at 700°C and 850°C, which contain calcium hydroxide ($Ca(OH)_2$) instead of sodium hydroxide (NaOH 45%) and cured in the curing room, the remaining specimens were casted into two sets of each. One set was cured at 60°C for (22 ± 2) hours and then moved to the curing room as shown in *figure 18*, while the other set was cured solely in the curing room.

The reason for curing at 60°C for (22 ± 2) hours is that based on common practice, geopolymer materials are typically cured at higher temperatures after mixing. Studies have shown that curing temperatures below 100°C are preferable for geopolymer materials, with some research suggesting a curing temperature range between 60°C and 80°C (17). By subjecting the specimens to this initial curing temperature, it allows for the geopolymerization process to begin and promotes the development of desirable properties in the clay-based geopolymer specimens.

Figure 18. shows curing of samples in the heating cabinet at 60°C for (22 ± 2) hours.

2.7 Testing procedure

The specimens were tested for flexural strength and compressive strength at 7 days ±2 hours and 28 days ±4 hours, respectively, in accordance with the NS-EN-196-1:2016 standard. For both the local marine clay and pottery white clay, the tests include a set of specimens that were placed in the heating cabinet at 60°C for (22 ± 2) hours, and another set of specimens that were not subjected to the heating cabinet. For the reference specimens and the specimens with calcium hydroxide ($Ca(OH)_2$), the tests included a set of specimens that were cured only in the curing room, as these materials were not placed in the heating cabinet. The instruments used for testing met the requirements specified in the NS-EN-196-1:2016 standard as shown in *figure 19-20.*
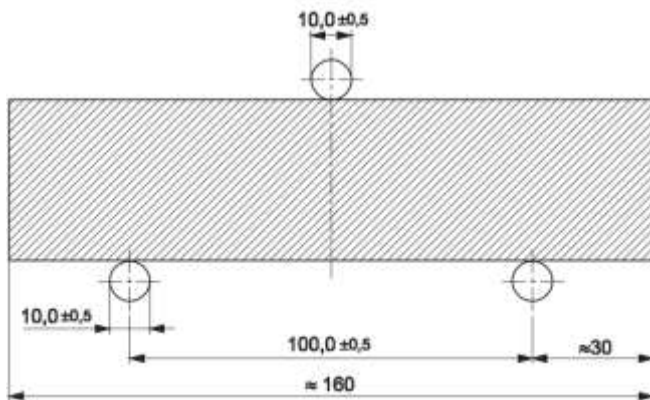

Figure 19. The flexural strength testing instrument. Source (NS-EN-196-1:2016)
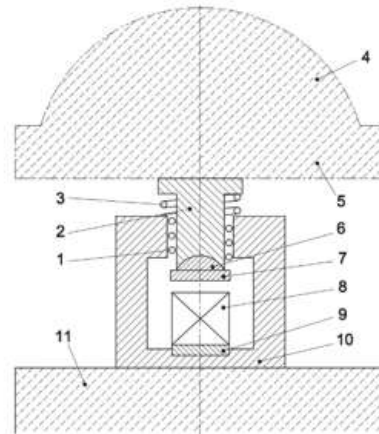

Figure 20. The compressive strength testing instrument. Source (NS-En-196-1:2016).

2.7.1 Flexural strength test

The flexural strength test was the first of the testing procedures, conducted in accordance with the requirements of the NS-EN-196-1:2016 standard. The maximum load was adjusted to 10kN, and the loading rate was set at 50 N/s. The specimens were taken to the testing room in sets of no more than two at a time in order to carry out the tests within 15 minutes of removing the specimens from the curing room and taking them out of the plastic bags. The procedure for testing includes the following steps: the specimen was taken out of the plastic bag, placed on the instrument, the glass door was closed and locked as a safety requirement of the testing machine as it is shown in the *Appendix A4*. Then, the program was started, and the graph displayed the amount of load required to break the specimen into two pieces (*see Appendix A5*), as
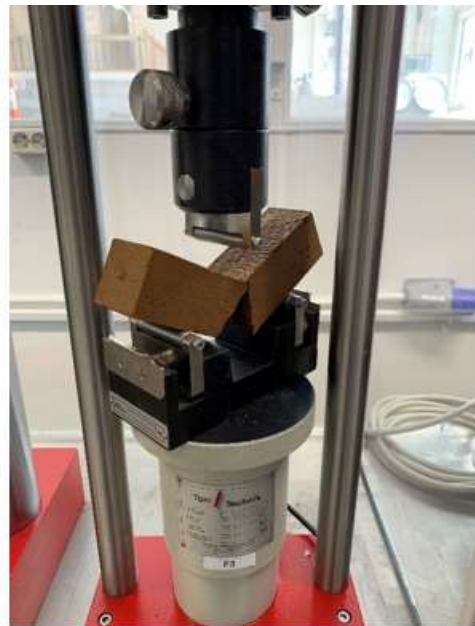

Figure 21. Shows the flexural strength test of local marine clay.

shown in *figure 21*. The results were noted down and the same procedure was repeated for all the specimens.

2.7.2 Compressive strength test

After the flexural test, the compressive strength test was performed on half of the test specimens that had been previously fractured during the flexural test. The compressive strength test was also performed in accordance with the NS-EN-196-1:2016 standard, where the maximum load was 300KN and load rate was adjusted to 2400 N/s. The procedure for testing includes the following steps: one half of each fractured specimen was placed on the testing instrument, as shown in the *figure 21,* the glass door was then closed, and the program was initiated to apply the load. The graph displayed the amount of load needed to fracture the specimen as it is shown *Appendix A5*. The results were recorded, and the same procedure was repeated for the remaining two half specimens of the same set and all the other sets of specimens.

Figure 22. Shows the compressive strength test of local marine clay.

2.7.3 Thermal and acid resistance test

Studies have shown that clay-based geopolymers, as well as geopolymers in general, exhibit high resistance against fire, thermal stress, and acidic attacks (6,27,28). Geopolymers are known for their excellent thermal stability and fire resistance properties, making them suitable for applications where exposure to high temperatures or fire hazards is a concern. The study conducted tests on test specimens made from local marine clay, pottery white clay, and a reference mixture containing standard cement to evaluate the response of these specimens to high thermal stress, simulating a fire scenario. The testing procedure was conducted in a controlled laboratory environment, ensuring safety precautions were in place. During the test, each specimen was subjected to high heat using a propane torch until a visible change or damage was observed as shown in *Figure 23*. The purpose of this approach was to determine the point at which the specimen exhibited signs of thermal degradation or structural failure due to the applied heat. The intensity and temperature of the torch were adjusted to be the same for all three tests, ensuring consistency in the applied thermal stress. The specimens were carefully observed and analyzed during the testing process. The use of a propane
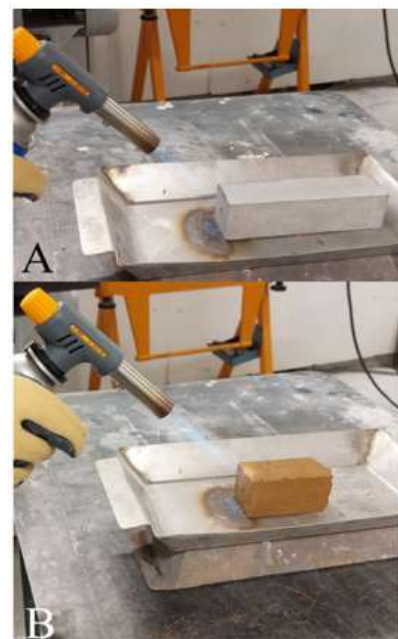

Figure 23. A. shows standard cement specimen and B. shows local marine clay exposed to propane flame.

torch allows for controlled and localized heating, simulating the effects of fire on the clay-based geopolymer specimens.

The final test conducted on the specimens involved subjecting the specimens to an acid test. Three samples, one made with local marine clay, one with pottery white clay, and one with standard cement (the reference), were immersed in a solution of hydrochloric acid (HCl 10%) for a duration of 48 hours, as shown in the *figure 24*. The aim of this test was to assess the resistance of the specimens to acidic conditions, and to simulate potential exposure to corrosive environments. During the 48-hour immersion, the specimens were monitored for visible sign of decoration after two hours, 24 hours and 48 hours. These tests provide valuable insights into the clay-based geopolymer materials ability to withstand acidic environments. The results contribute to evaluating their suitability for various applications in settings where acid exposure is likely to occur.
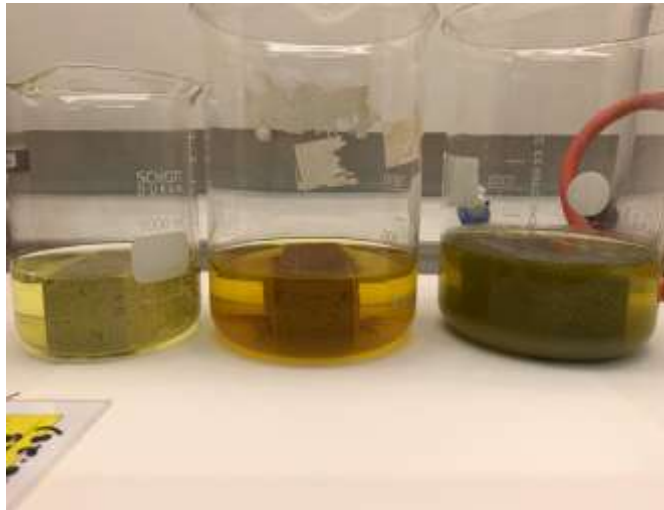

Figure 24. Shows the three specimens immersed into the hydrochloric acid (HCl 10%) solution for 48 hours.

3. Results

A comprehensive set of tests was conducted to evaluate the properties of the specimens. These tests included flexural strength and compressive strength measurements at 7 and 28 days to assess the mechanical performance. Additionally, fire and thermal resistance tests were carried out to evaluate the clays' ability to withstand high temperatures compared to the reference material. Furthermore, an acid test was conducted to evaluate the resistance of the specimens to acidic environments compared to the reference specimen. These set of testes offered a valuable understanding of the properties and performance of the clay-based geopolymer. The examination into various factors, including mechanical strength, thermal resistance, and acid resistance, helped to obtain a valuable insight into the behavior, capabilities, weakness, and suitability of clay-based geopolymer as a potential substitute for cement and other geopolymers in concrete.

The calculations for both flexural strength and compressive strength were performed according to the formula specified in the NS-EN-196-1:2016 standard *(equation 3.1).* The standard provided the guidelines and equations necessary to accurately determine the strength properties of the tested specimens, which ensures accuracy and consistency.

Flexural strength R_f   *Compressive strength R_c*

$$R_f = \frac{1{,}5 \times F_f \times l}{b^3} \qquad\qquad R_c = \frac{F_c}{1600} \qquad\qquad (3.1)$$

3.1 Flexural strength

The results of the flexural strength tests show that the specimens made with standard cement (reference specimens) exhibited the highest strength, which is expected considering the known strength characteristics of cement-based materials. However, it is noteworthy that both the local marine clay and pottery white clay specimens displayed such significant lower flexural strength across all three calcination temperatures, which was unexpected as it shown in *figure 25-26*. Another noteworthy observation is the absence of a direct correlation between the calcination temperature and the flexural strength development in this study. This results contradict the results of previous studies, which indicate that an optimal calcination temperature range of 800°C to 950°C is often associated with improved properties for illitic clay-based material (23,24).

Although it is worth noting that the previous point about the lack of correlation between calcination temperature and strength development applies to the local marine clay used in this study, as it contains a relatively high percentage of illite (23%) (12). However, it is not possible to draw the same conclusion for the pottery white clay due to the limited information available about its mineralogy and the absence of data regarding the amount and presence of illite or other clay fractions in its minerals. The results also show a clear correlation between curing time (7 days and 28 days) and the development of strength for both local marine clay and pottery white clay specimens *(see Figure 25-26).* As expected, the strength of the specimens increased after 28 days of curing compared to 7 days for all three calcination temperatures. Among the different calcination temperatures, the local marine clay specimens that were calcined at 850°C and cured without the heating cabinet show the highest strength development, with an improvement of 250% (0,06-021) MPa

(*see figure 25*). Similarly, the specimens that cured in the heating cabinet at 60°C for (22 ± 2) hours also exhibit an increase in strength, with an increase of 33% (0,09-012) MPa.
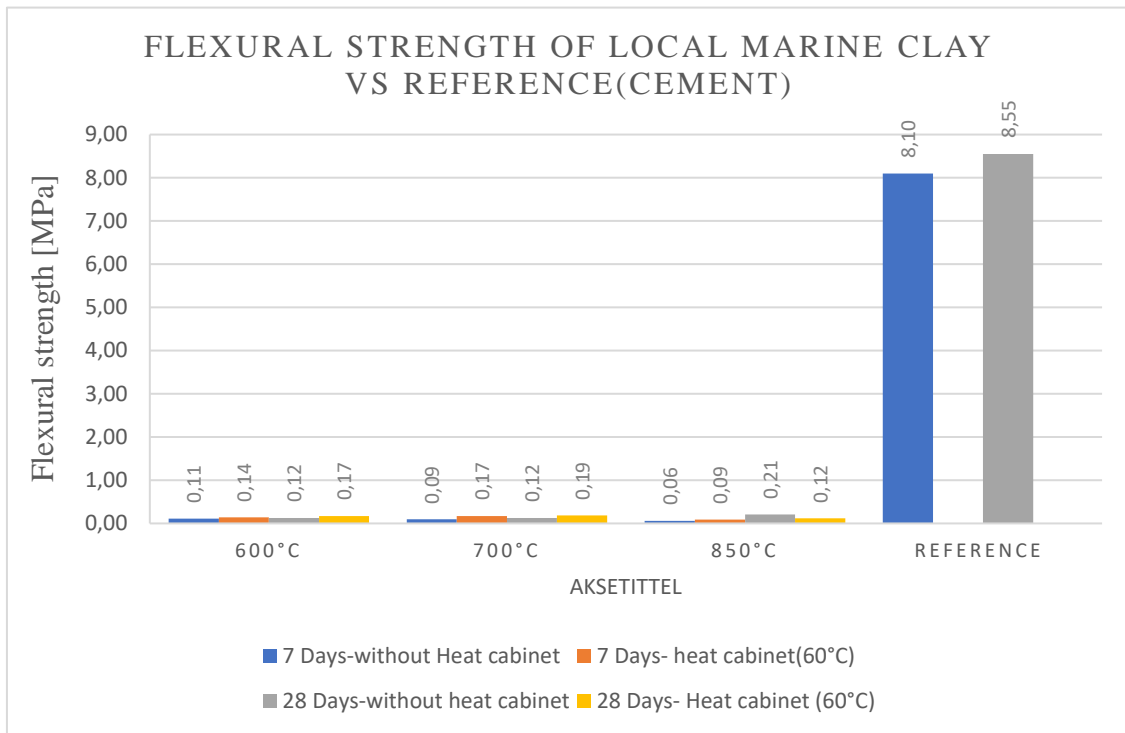

Figure 25: The 7-28 days flexural strength development of local marine clay with different calcination temperatures (600, 700, and 850) °C, and with and without heating cabinet at 60°C for (22 ± 2) in comparison to the flexural strength of standard cement(reference).
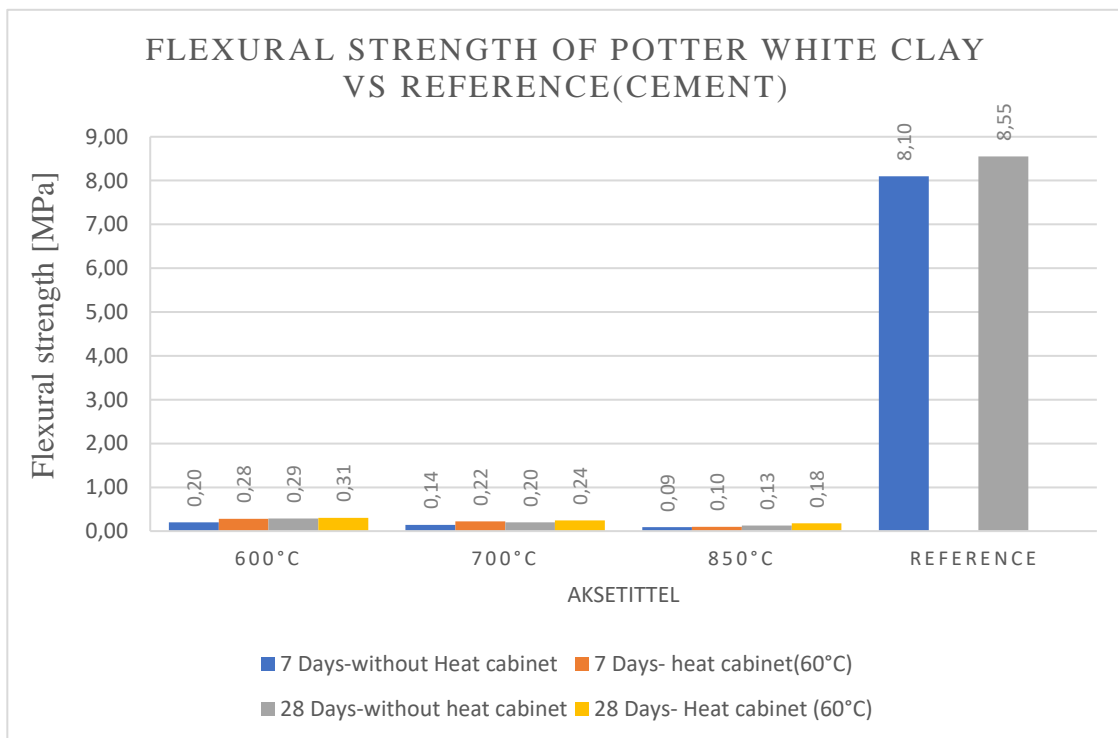

Figure 26. The 7-28 days flexural strength development of pottery white clay with different calcination temperatures (600, 700, and 850) °C, and with and without heating cabinet at 60°C for (22±2) in comparison to the flexural strength of standard cement(reference).

The results of this study also indicate that the specimens cured at 60°C for (22 ± 2) hours in the heating cabinet exhibited higher strength at both the 7-day and 28-day tests for both local marine clay and pottery white clay. This finding is consistent with the existing literature, which suggest that curing geopolymers at higher temperatures, including temperatures around 60°C, can lead to improved strength development (24). However, an interesting deviation from the previous studies was observed in the case of the local marine clay calcined at 850°C, which the 28-day strength development without the heating cabinet was higher than that of the sample cured in the heating cabinet at 60°C for (22 ± 2) hours.

3.2   Effect of calcium hydroxide

When it comes to the flexural strength results of the two local marine clay specimens (700°C and 850°C) which were proportioned and casted with 11.5% and 10% calcium hydroxide ($Ca(OH)_2$) respectively instead of sodium hydroxide (NaOH 45%), show a similar low flexural strength as the local marine clay and pottery white clay specimens that were casted without calcium hydroxide ($Ca(OH)_2$). The addition of calcium hydroxide does not seem to significantly improve the flexural strength of the clay-based geopolymer specimens as it can be seen in *figure 27*. When it comes to the curing time (7 days-28 days) and strength development, the clays show a slightly increase in strength. Although it is worth noting that the local marine clay calcined at 850°C and proportioned with 10% calcium hydroxide ($Ca(OH)_2$) has developed a higher flexural strength compared to the clay calcined at the same temperature but with 11.5% $Ca(OH)_2$. This finding is unexpected considering the higher amount of calcium hydroxide present in the latter clay mixture.
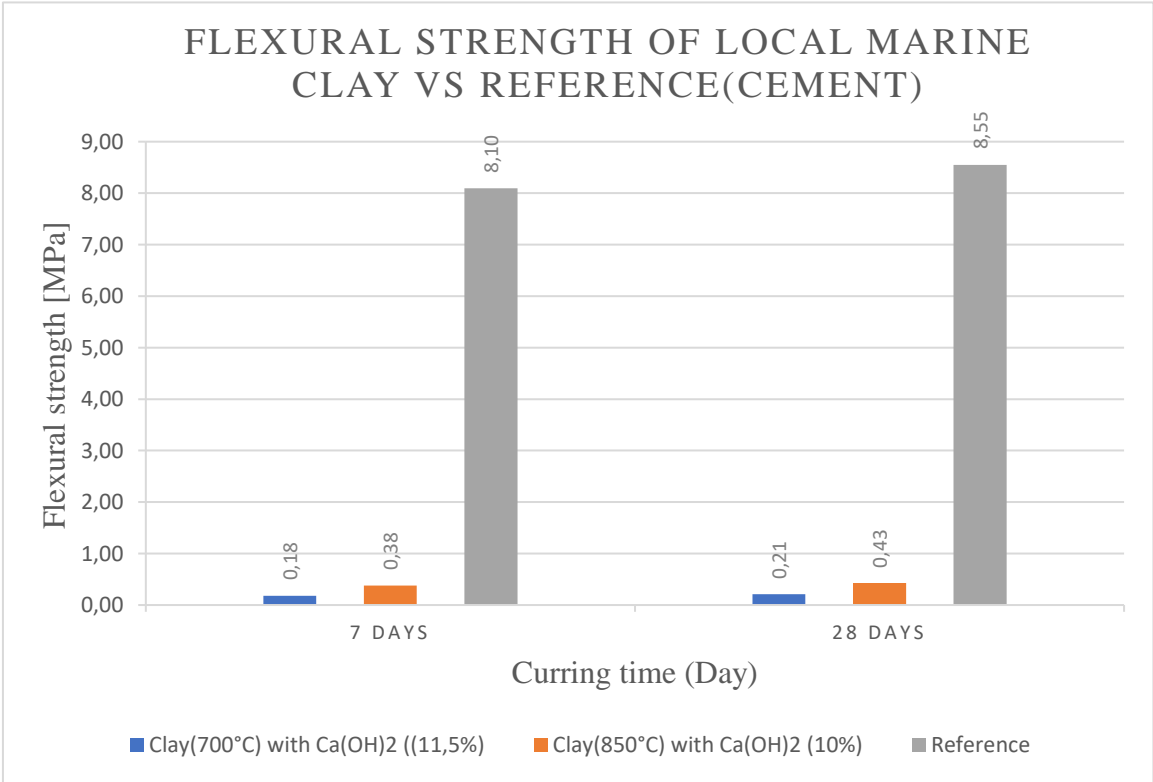

Figure 27. The 7-28 days flexural strength development of local marine clay calcined at (700 and 850) °C which are proportioned with calcium hydroxide ($Ca(OH)_2$) instead for sodium hydroxide (NaOH 45%) in comparison to the flexural strength of standard cement(reference).

3.3 Compressive strength

The results of the compressive strength tests align with the findings of the flexural strength tests. The specimens made with standard cement (reference) demonstrate the highest compressive strength, while the local marine clay, pottery white clay, and specimens casted with calcium hydroxide exhibit significantly lower compressive strength development in comparison to the reference specimens as it is shown in *figure 28*. As in the flexural strength, contrary to expectations and previous studies, the results do not indicate any correlation between the calcination temperature (600°C, 700°C, and 850°C) and the strength development in the local marine clay *(see figure 28)*. Previous research has suggested that illitic clays have improved properties when calcined at higher temperatures, typically ranging from 800°C to 950°C (23,24). However, in this study, the strength development in the local marine clay did not show a clear relationship with the calcination temperature within the tested range.
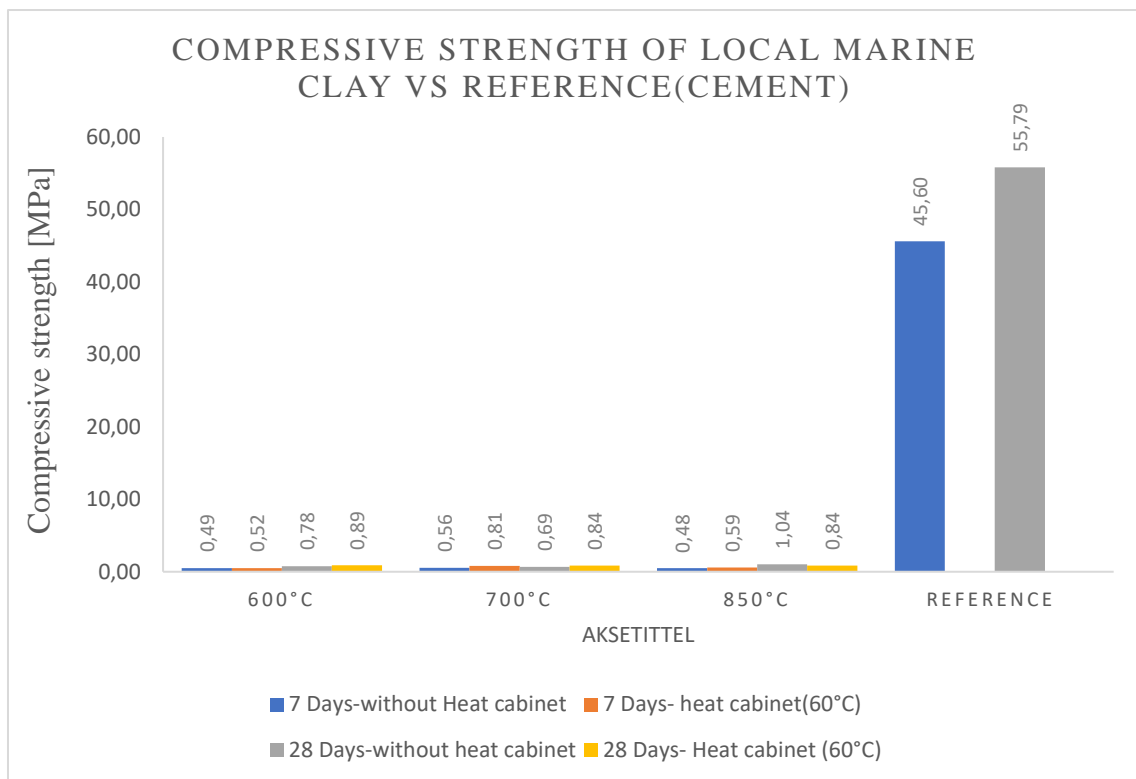

Figure 28. The 7-28 days compressive strength development of local marine clay with different calcination temperatures (600, 700, and 850) °C, and with and without heating cabinet at 60°C for (22 ± 2) in comparison to the flexural strength of standard cement(reference).

Although, the results show an increase in strength with curing time (7 days- 28days) at all three calcination temperatures with highest strength development at 850°C calcination temperature as shown in *figure 28-29*. Similar to the findings on flexural strength development, the results of this study demonstrate that the specimens cured at 60°C for (22 ± 2) hours in the heating cabinet before transferring to the curing room exhibited higher strength in both the 7-days and 28-days tests compared to the specimens which were cured only in the curing room. This observation is consistent with previous studies (17) that suggest curing geopolymers at higher temperatures, such as 60°C, can contribute to improved strength development. However, it is worth noting that, similar to the flexural strength results, the clay calcined at 850°C showed a deviation from the expected trend,

where the 28-day strength development without the heating cabinet was higher than that of the sample cured in the heating cabinet at 60°C for (22 ± 2) hours.

When examining the results for pottery white clay, there is a correlation between the curing time (7 days - 28 days) and the strength development. The compressive strength of the specimens shows an increase at the 28-day testing compared to the 7-day testing, which suggests that the curing time plays a role in the strength development of pottery white clay-based geopolymers (*see figure 29*). As regarding to the correlation between calcination temperature (600°C, 700°C, and 850°C) and the strength development, the results show that highest strength development occurs at the clay calcined at 700°C.

Similar to the local marine clay, the specimens cured at 60°C for (22 ± 2) hours in the heating cabinet before transferring to the curing room exhibited higher strength in both the 7-day and 28-day tests compared to the specimens which were cured only in the curing room, accept the clay calcined at 850°C, which deviates from this trend.
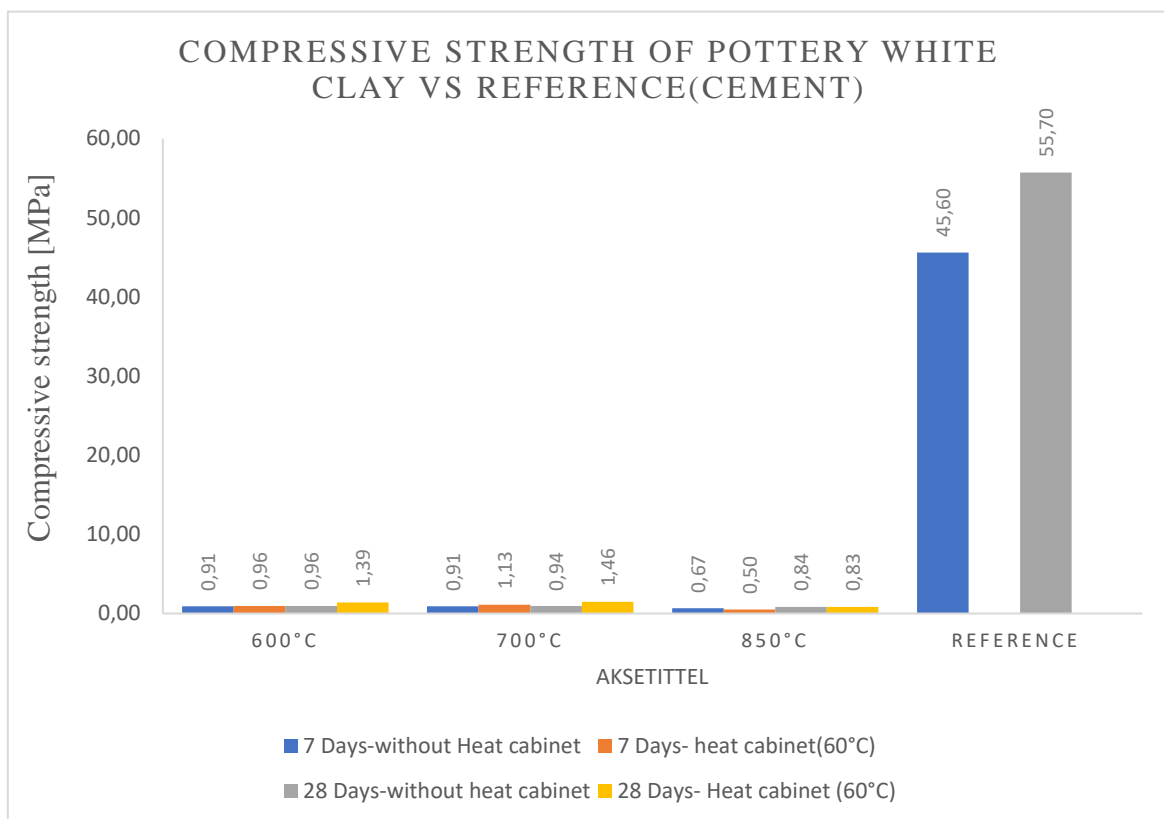

Figure 29. The 7-28 days compressive strength development of pottery white clay with different calcination temperatures (600, 700, and 850) °C, and with and without heating cabinet at 60°C for (22 ± 2) in comparison to the flexural strength of standard cement(reference).

3.4 Calcium hydroxide

The results obtained for the compressive strength of the local marine clay specimens, which were calcined at 700°C and 850°C and incorporated 11.5% and 10% calcium hydroxide (Ca(OH)$_2$) respectively instead of sodium hydroxide (NaOH 45%), indicate significantly

lower strength values compared to the reference specimens in both the 7-day and 28-day tests, which similar to the compressive strength of local marine clay and pottery white clay *(se figure 30)*. This observation is consistent with the trends observed in the compressive strength of the local marine clay and pottery white clay specimens. It is worth mentioning that the compressive strength results show a higher value for the clay specimens with 11.5% calcium hydroxide ($Ca(OH)_2$) compared to the specimens with 10% $Ca(OH)_2$, which contradicts the flexural strength results obtained from the same set of specimens, where the clay with 10% $Ca(OH)_2$ exhibited higher flexural strength.

COMPRESSIVE STRENGTH OF LOCAL MARINE CLAY VS REFERENCE(CEMENT)
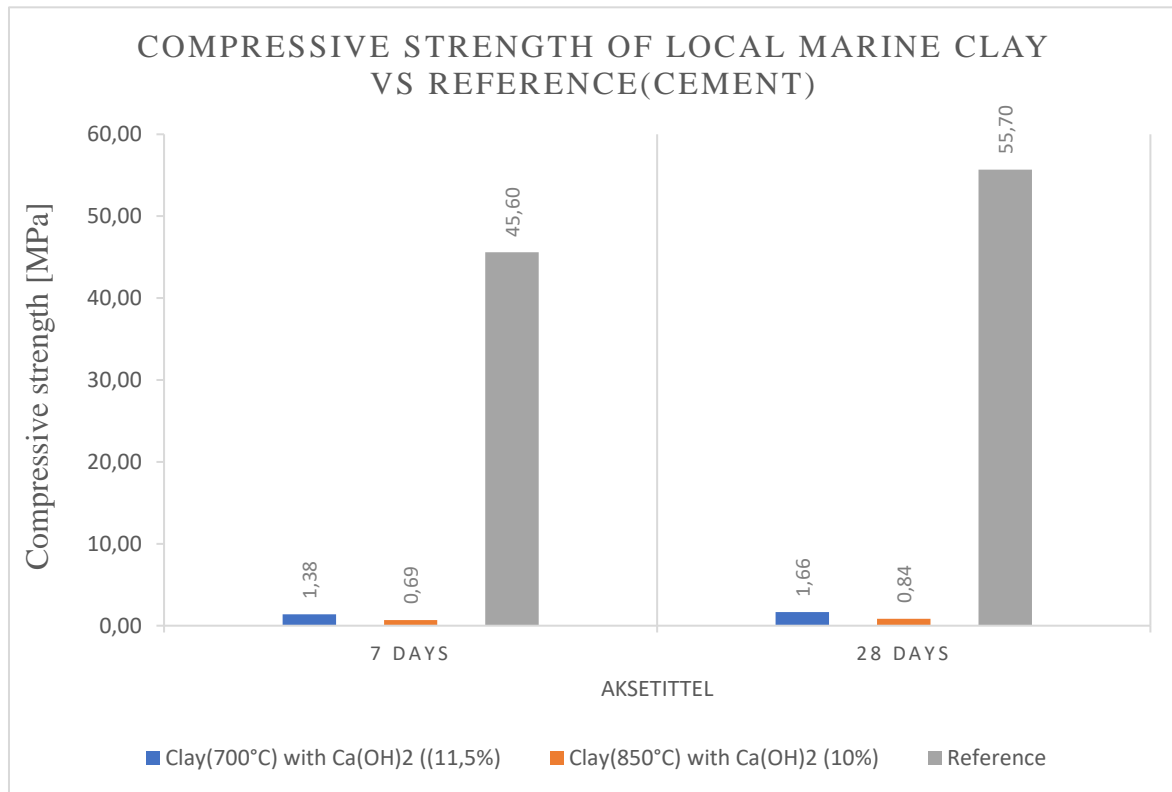
Figure 30. The 7-28 days compressive strength development of local marine clay calcined at (700 and 850) °C which are proportioned with calcium hydroxide ($Ca(OH)_2$) instead for sodium hydroxide (NaOH 45%) in comparison to the flexural strength of standard cement(reference).

3.5 Fire and thermal resistance

The results of the thermal resistance test indicate that local marine clay has the highest resistance to thermal stress compared to pottery white clay and standard cement. Figure *31A* shows the condition of local marine clay specimen after being exposed to a propane flame for more than 3 minutes, illustrates its ability to withstands the heat. *Figure 31C* shows the pottery white clay after being subjected to propane flame for around 1 minutes and lastly *figure 31A* shows the reference specimen (standard cement) after being subjected to the same propane flame for just 30 seconds.

This visual evidence demonstrates the superior thermal resistance of the clay-based geopolymers in this case local marine clay and pottery white clay compared to the standard cement, which is consistent with the literature about the high thermal resistance of clay-based geopolymers (27,28).
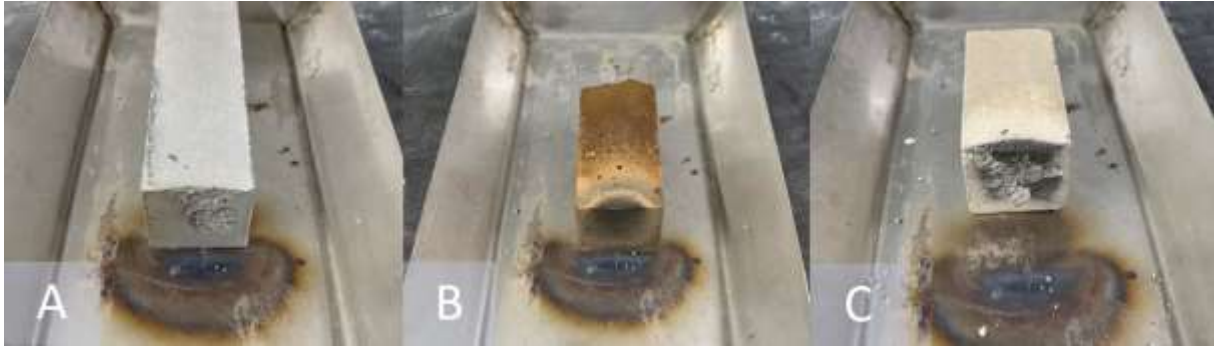
Figure 31. A: Standard cement after 30 second exposer to propane flame. B: local marine clay after 3 minutes exposer to propane flame. C: pottery white after 1 minute exposer to propane flame.
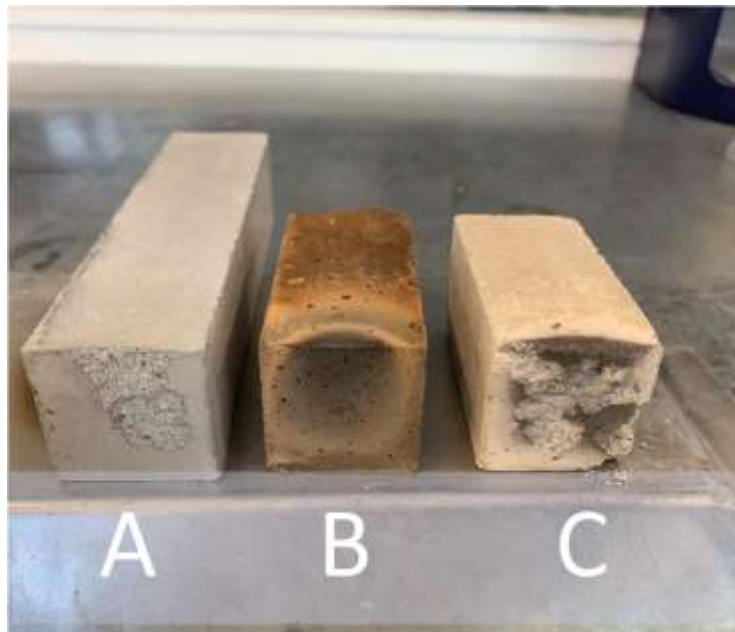

Figure 32. shows the compression of the three samples after exposer to the propane flame from right to left: A. Standard cement, B. local marine clay and C. pottery white clay.

3.6 Acid test

The acid test conducted in this study involved submerging the test specimens in hydrochloric acid (HCl 10%) solution for a duration of 48 hours. The results obtained from the acid test show the ability of the clay-based geopolymer materials to withstand acidic environments and reveal that both the local marine clay and pottery white clay specimens have superior resistance to the acidic environment compared to the standard cement specimen as it is evident in *figure 33*. This observation is in line with previous studies and literature on the subject, which suggest that clay-based geopolymer materials have inherent resistance to acidic conditions (3,6,27,28).
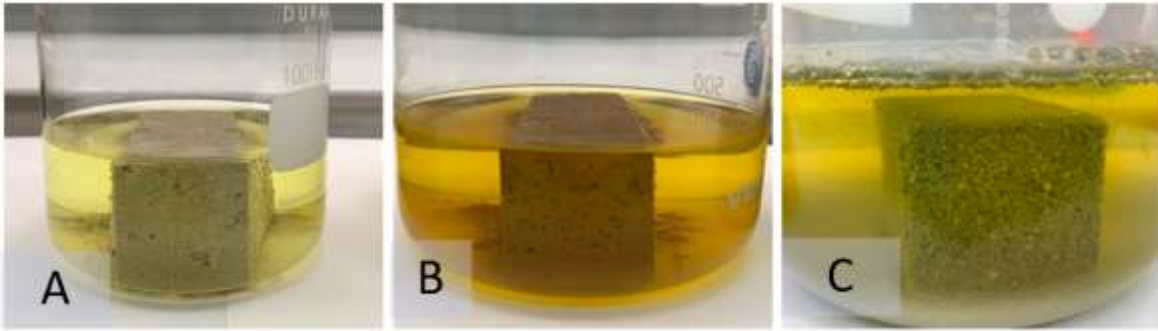
Figure 33. Effect of hydrochloric acid (HCl 10%) on the samples after 48 hours. A. shows the pottery white clay sample, B. shows the local marine clay sample and C. shows the standard cement sample.

4.   Discussion

4.1   Flexural and compressive strength

The results of the flexural and compressive strength tests clearly distinguish between the strength of local marine clay, pottery white clay, and the standard cement (reference). As anticipated, the standard cement (reference) showed the highest strength, which is consistent with the well-known strength properties of cement materials. However, the clay specimens displayed a significantly low flexural and compressive strength, which was unexpected *(see Figures 25, 26, 28 and 29).* This significant discrepancy in strength values indicates that clay materials have limitations in terms of flexural strength when compared to standard cement. Which raises concerns regarding the suitability of these clay materials as complete and 100% replacements for cement in concrete.

The absence of direct correlation between calcination temperature and the flexural strength development contradicts the findings of previous studies and existing literature which suggest that the optimal calcination temperature for illitic clays is between 800°C to 950°C (1,2). An explanation for this contradiction could be attributed to the composition of the local marine clay used in the study. It was found that the clay contained only 23% illite(12), which may not be sufficiently high to generate a significant difference when it is calcined at the optimal temperature as suggested in existing literature. Another factor that could have influenced the results is the presence and quantity of other clay fractions, such as a high amount of biotite (26%), 16% chlorite, 13% plagioclase, 7% amphibole, 7% quartz, and 4-6% potassium feldspar (12). Each of these clay fractions may have reacted unfavorably to any of the three different calcination temperatures, as a result hindering the development of high flexural strength for the clay as a whole.

One significant factor that may have had a substantial impact on the clay's strength characteristics is the amount of clay used as the binder in the study. The study focused on using only calcined clay as the sole binder in the mortar, without blending it with any percentage of Fly Ash (FA), Slag, or cement, which is the main objective of the study. Typically, in concrete mixes, one or a combination of these materials is present in a range of over 60%, mixed with the calcined clay as the binder. The absence of these materials in the binder may have overshadowed the effect of the calcination temperature, thereby affecting the overall strength of the clay specimens.

However, it is important to note that the explanation about amount and presence of illite or other clay fractions is valid for the local marine clay, it cannot be applied for the pottery white clay, due to the limited available information about the mineralogy of the pottery white clay, as mentioned in the previous chapter.

4.2   Curing time

Both types of clays show an increase in both flexural and compressive strength from 7 days of curing to 28 days, which is not surprising. However, it is important to note that the correlation trend differs between local marine clay and pottery white clay in terms of the percentage of increase and the calcination temperature at which the increase occurred. For local marine clay, the highest increase occurs at the 850°C for both flexural and

compressive strength, which can be related to the presence of relatively high amount of illite among the clay fractions. For the pottery white clay, the highest increase occurs at 600°C for the flexural strength and at 850°C for the compressive strength, which is difficult to provide a specific explain for this trend, due to the lack information about its mineralogy. This difference in behavior between the two clay types highlights the complexity and variability of clay-based geopolymers in terms of performance and the importance of their composition and mineralogy.

4.3   60°C heating cabinet

The results of flexural and compressive strength tests of both clays indicate that curing the specimens at higher temperature, in this case 60°C for (22 ± 2) hours leads to development higher strength, which is expected and is consistent with the findings of precious studies, which indicate that curing geopolymers at a higher temperature after mixing is preferable (17). While different studies suggest different curing temperatures, some propose a curing temperature around 60°C (17). However, as the results show, local marine clay calcined at 850°C deviates from the previous studies, where 28-days flexural and compressive strength development without the heating cabinet is higher than that of the sample cured in the heating cabinet at 60°C for (22 ± 2). In case of pottery white clay, similar deviation is observed at 850°C calcination temperature, where the compressive strength of both 7- and 28-days of samples cured without heating cabinet is higher than of those cured in the heating cabinet at 60°C for (22 ± 2) hours. These unexpected deviations in curing behavior of the 850°C calcination temperature highlights the complexity of clay-based geopolymers and suggest that both local marine clay and pottery white clay used in this study, when calcined at higher temperature(850°C) may exhibit unique response to curing conditions, which emphasize the need for more detailed studies to better understand the optimal curing condition and temperature of these materials.

4.4   Effect of calcium hydroxide

The results of the two sets of specimens, in which sodium hydroxide (NaOH 45%) was replaced with calcium hydroxide (Ca(OH)$_2$), show no significant change in flexural and compressive strength compared to the sets of clay that were proportioned and casted without calcium hydroxide. These results indicate that the addition of calcium hydroxide (Ca(OH)$_2$) does not have a significant effect on the mechanical performance of the clay.

This lack of significant effect can be related to the relatively low dosage of 10-11.5% calcium hydroxide used in the mix. Another, and perhaps more plausible explanation for this result might be the use of calcined clay as the sole binder, which is main propose of this study. As mentioned earlier in the chapter, using calcined clay as the sole binder in the mix results in very low mechanical strength, and the additional calcium hydroxide does not have a strong enough influence to cause any substantial changes.

The results also indicate a difference between the flexural strength and compressive strength of the specimens. In terms of flexural strength, the specimens with 10% calcium hydroxide show higher strength development at both 7 and 28 days. However, in terms of compressive strength, it is the opposite. Several factors may have influence on the mechanical strength of these specimens, including water-to-binder ratio (w/b-ratio) and

calcination temperature. The difference in w/b-ratio between the specimens with 10% calcium hydroxide (0,96) and those with 11,5% calcium hydroxide (0,82) may have an influence on their mechanical strength development. Another factor that could have an influence is the calcination temperature. The specimens with 10% calcium hydroxide were calcined at 850°C, while the specimens with 11,5% calcium hydroxide had a calcination temperature of 700°C. This difference in calcination temperature might have also influenced the flexural and compressive strength development in these specimens.

4.5 Fire and thermal test

The images obtained from the fire and thermal test provide valuable insights into the behavior of calcined clay and standard cement while being exposed to extreme heat. The local marine clay specimen shows an exceptional thermal resistance. Even after more than 3 minutes of being directly exposed to the propane flames. It shows minimal to no sign of damage which indicates that local clay material is capable of withstanding high temperature, which consistence with the existing literature in this area.

On the other hand, pottery white clay shows relatively lower, but still good thermal resistance compared the standard cement. Signs of peeling appears after 1 minute for the pottery white clay. Although it appears to have less resilient than local marine clay, it still possesses a good degree of thermal resistance, which again confirms the results of existing litterateur about the thermal resilient of clay-based geopolymers.

While the standard cement shows the lowest thermal resistance compared to the clay materials, this result is not surprising. As expected, the standard cement starts showing signs of peeling and damage after just 30 seconds of being exposed to the same propane flames. This indicates its low thermal resilience, which is align with the findings of previous studies.

4.6 Acid test

After been submerged in hydrochloric acid (HCl 10%) solution for 48 hours, both clay samples show a clear advantage over the standard cement sample. The clay samples show no sign of deterioration, whereas the standard cement clay shows a clear sign of deterioration. These results are consistent with findings of previous studies which indicate the incredible characteristic of clay-based geopolymers when exposed to acids (28). These findings demonstrate the remarkable ability of clay materials to withstand acidic exposure, making them very desirable in the construction industry where encountering acidic environments is very common. This is a desirable characteristic for various applications such as chemical plants, wastewater treatment facilities and other acidic environments.

5. Conclusion

In this study, flexural and compressive properties of local marine clay and pottery white clay were investigated and compared to the standard cement(reference). Additionally, their thermal and acid resistance have been assessed. The main objective of this study was to evaluate the viability of local marine clay as the sole binder to replace standard cement and other supplementary material such Flay ash (FA) and Slag in concrete.

Through a series of experimental methods, the two types of clays were calcined in three different temperatures (600, 700 and 850) °C, proportioned with addition of alkaline activators, such as NaOH (45%), Na_2SiO_3 (35%) and $Ca(OH)_2$. Two sets of each sample were casted, one was cured in heating cabinet at 60°C for (22 ± 2) hours, while the other one was cured solely in the curing room at (20 ± 1) °C with a relative humidity (RH) of (70 ± 2) %. After 7 and 28 days of curing, the samples were tested for flexural and compressive strength and compared to the samples made of standard cement(reference). The sample were also subjected to thermal and acid resistance testes to assess their performance in harsh conditions.

The results of flexural and compressive strength tests indicate that both local marine clay and pottery white clay exhibit significantly low mechanical strength compared to the standard cement(reference). The results also demonstrate that the calcination temperature does not have any significant impact on the development of the mechanical strength in either clay types. Furthermore the replacement of sodium hydroxide (NaOH 45%) with calcium hydroxide ($Ca(OH)_2$) does not show any significant effect on the mechanical strength of the local marine clay.

However, the thermal and acid resistance tests demonstrate that clay-based materials have a superior fire resistance and exceptional ability to withstand high acid attacks compared to the standard cement. These findings show the potential advantages of the clay-based geopolymers in environments where acid and fire resistance are important factors.

Based on these results, it is concluded that the local marine clay and pottery white clay may not possess the desired flexural and compressive characteristics required to be used as the sole binder to replace standard cement or other supplementary materials such as Fly Ash (FA) and Slag in concrete. The low mechanical strength observed in both clay types in this study raises the concern about the suitability of the clay-based materials as complete and 100% substitutes for standard cement in concrete industry. However, it is important to acknowledge the potential benefits of the clay-based materials in certain applications where their thermal and acid resistance properties are advantages.

In conclusion, this study provides valuable insight into the mechanical performance of local marine clay and pottery white clay calcined in three different temperatures as the sole binder in concrete. Although these materials may not be suitable to completely replace the standard cement in concrete, their exceptional ability to withstand high thermal load and acid attacks make them worthy of further investigations.

6. Suggestions for further studies

Investigate and explore the relationship between clay mineralogy and alkaline activation. It can be investigated to understand how different clay fractions respond to varying amounts and types of alkaline activators. This can involve studying the interaction between clay minerals and alkaline solutions to determine the optimal activator composition for different clay types. The aim would be to identify the most effective activators that enhance the reactivity and performance of clay-based materials.

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Appendix

A1

Figure 34. The grinding machine utilized in this project is owned by SENTIF and was the only available grinding machine at the NTNU during the study.

Figure 34. The grinder used in this project.

A2

Figure 35. The image shows the local marine clay undergoing the cooling process in room temperature following the calcination stage. The image provides a visual depiction of the color transformation that occurs in the local marine clay during the calcination process.

Figure 35. The cooling process of clay.

A3

The image provides a glimpse into the curing process of the mortars done in the study. It shows a combination of newly cast samples that are still inside the moulds and other samples that have been demoulded and placed inside plastic bags for further curing. The curing environment for these samples is a designated curing room with controlled conditions. The temperature is maintained at (20 ± 1) °C, ensuring a consistent and optimal curing temperature. The relative humidity (RH) is also controlled at (70 ± 2) %, creating a suitable moisture environment for the curing process, even though the samples are covered with plastic bags before demoulding and are placed inside plastic after demoulding to ensure there is no loss of moisture.

Figure 36. Samples in curing room.

A4

These graphs offer valuable insight and serve as visual representations of the mechanical data obtained from the conducted tests. The graphs her provide a clear and concise overview of the amount of load necessary to fracture the samples during the test (page 2-3). The other important information that presented here is the speed of machine for the compressive test which is 2400N/s (page 1) which is consistent with the requirements of the standard NS-EN-196-1:2016.

Toni / Technik

Print date: 07.06.23

Test report

Test protocol :   Test standard :
Tester   :   Machine data : III [10kN]
Customer   :
Test speed : 2400 N/s

Test results:

Sub-series 1		ID
Legend	No.	
	1.1	Sement_referanse_1
	1.2	Sement_referanse_2
	1.3	Sement_referanse_1
	1.4	Sement_referanse_2
	⊘ 1.5	Sement_referanse_2
	1.6	Sement_referanse_trykk_2
	1.7	Sement_referanse_2

Mørteltesting_3pkt .zs2   **Page1/3**

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Legend	Sub-series 1 No.	Date/Clock time	a mm	b mm	h mm	S₀ cm²
	1.1	4/21/2023 10:39:52 AM	40.0	40.0	40.0	16.00
	1.2	4/21/2023 10:43:38 AM	40.0	40.0	40.0	16.00
	1.3	4/21/2023 10:47:42 AM	40.0	40.0	40.0	16.00
	1.4	4/21/2023 10:50:58 AM	40.0	40.0	40.0	16.00
⊘	1.5	~~4/21/2023 10:54:42 AM~~	40.0	40.0	40.0	~~16.00~~
	1.6	4/21/2023 10:55:16 AM	40.0	40.0	40.0	16.00
	1.7	-	40.0	40.0	40.0	-

Legend	Sub-series 1 No.	m kg	ρ g/cm³	σ_M MPa	F_{max} kN
	1.1	0.5	1.953	8.13	3.4689
	1.2	0.5	1.953	8.06	3.4404
	1.3	0.5	7.813	46.20	73.9245
	1.4	0.5	7.813	44.99	71.9893
⊘	1.5	~~0.5~~	~~7.813~~	-	-
	1.6	0.5	7.813	43.83	70.1289
	1.7	0.5	-	-	-

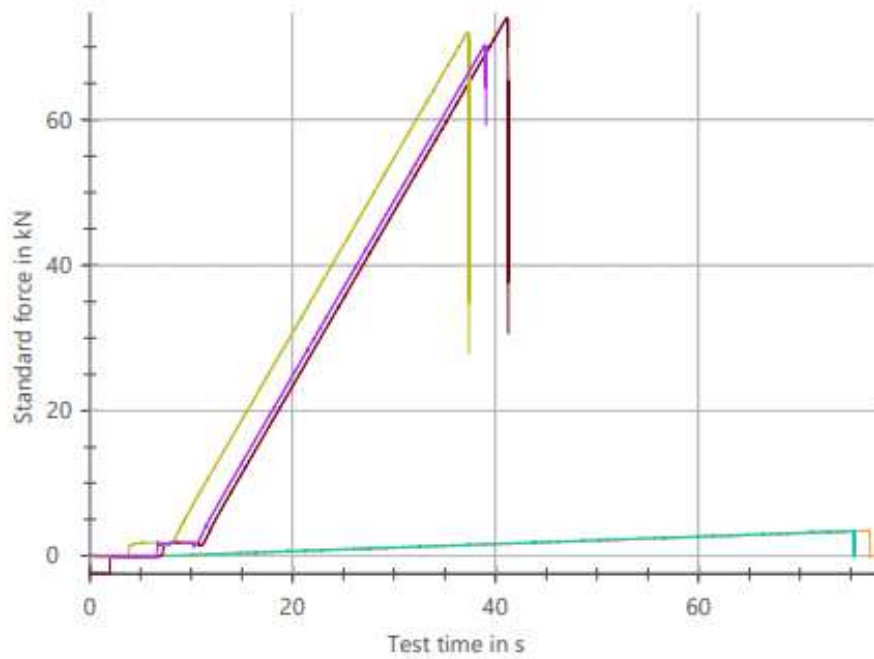| Sub-series 1	a mm	b mm	h mm	S₀ cm²	m kg	ρ g/cm³	σ_M MPa	F_{max} kN
n = 5								
x̄	40.0	40.0	40.0	16.00	0.5	5.469	30.24	44.5904
s	0.0	0.0	0.0	0.00	0.000	3.209	20.23	37.5756
v [%]	0.00	0.00	0.00	0.00	0.00	58.68	66.91	84.27
n	5	5	5	5	5	5	5	5

Toni / Technik

Series graph:

Figure 37. Graphs from mechanical tests

A5

These images serve as valuable visual representations of the mechanical testing process, providing a clear understanding of the behavior exhibited by the various specimens during the test. They effectively highlight the difference between the materials being tested, allowing for direct observation of their response to applied forces, including deformations and fracture patterns. By comparing the images of the standard cement specimen(reference) with those of the local marine clay and pottery white clay specimens, one can clearly observe the contrasting behaviors exhibited under load. The inclusion of these visuals provides a better understanding of the behavior and characteristics of the materials used in this study under load and during the testing process.
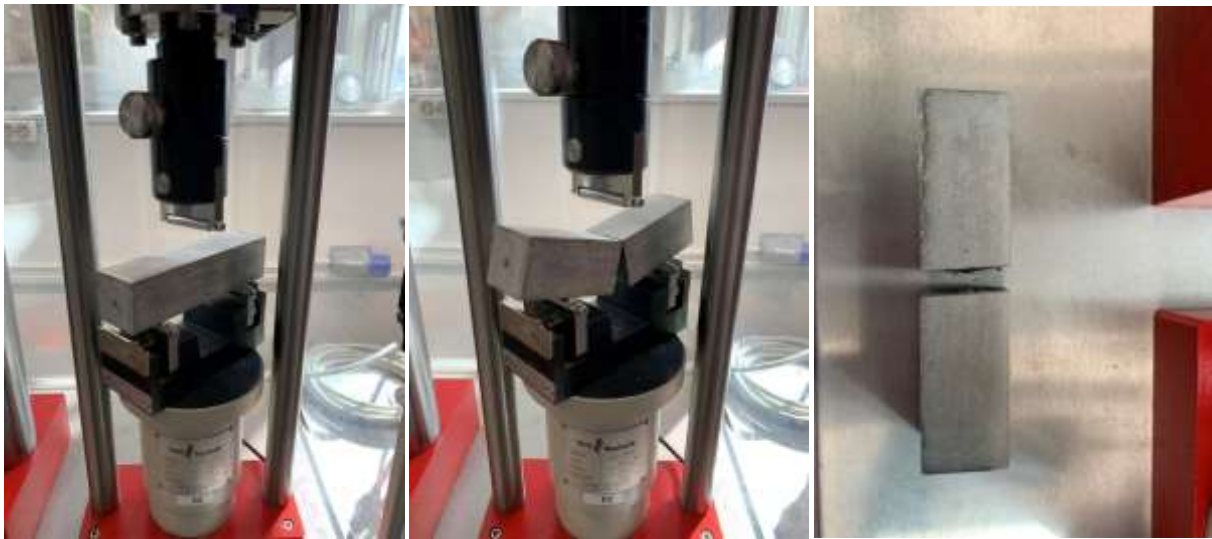
Figure 38. Standard cement specimen(reference) during the flexural test

Figure 39. Local marine clay specimen during the flexural test
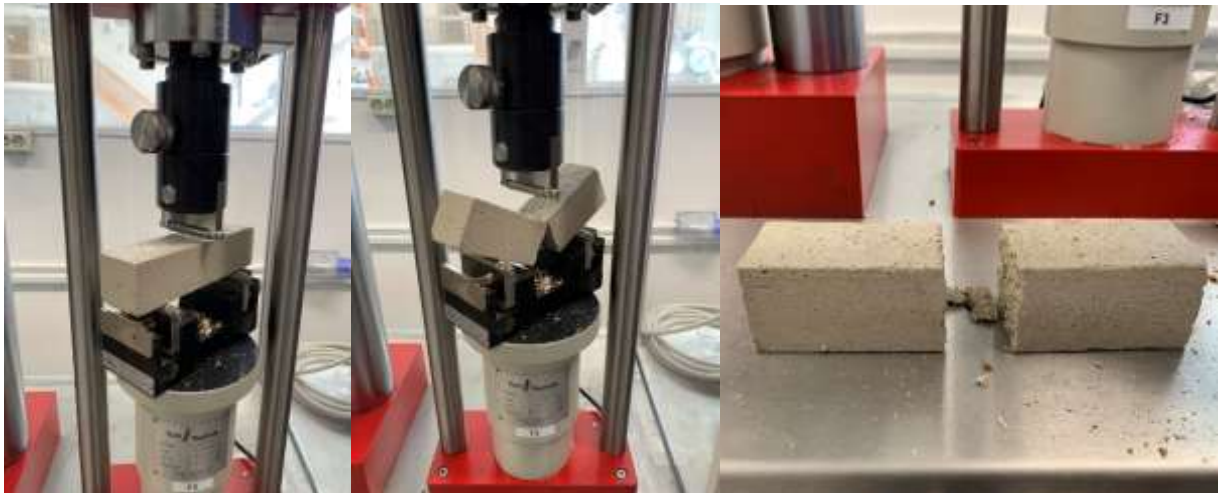
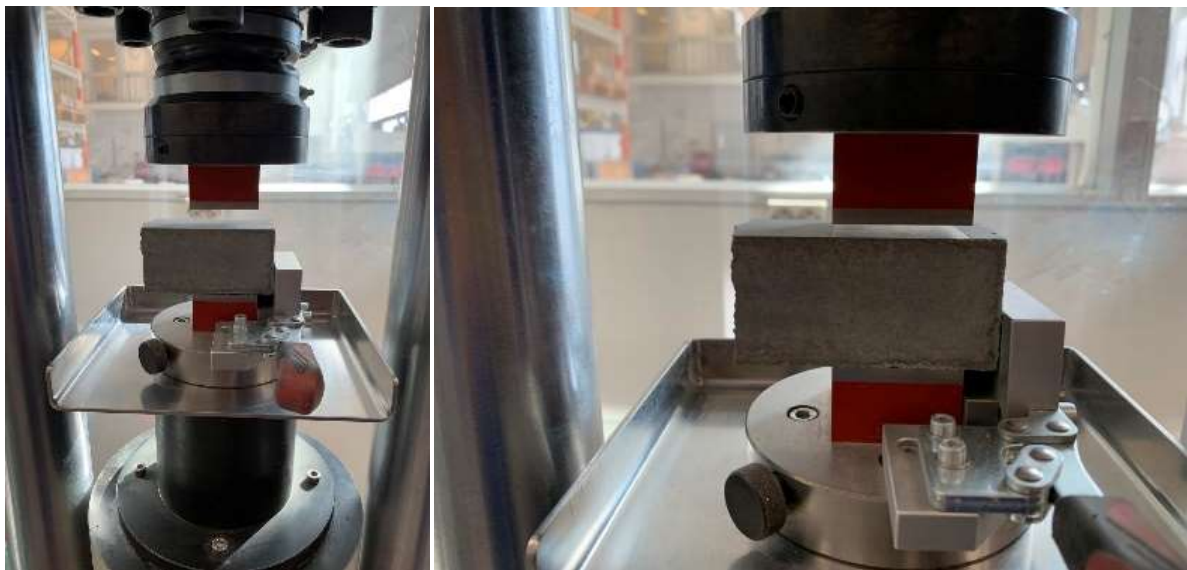*Figure 40. Local marine clay specimen during the flexural test*

Figure 41. Standard cement specimen(reference) during the compressive strength test. Image on the right shows the specimen before the load is applied and image on the left shows the fractured specimen after the load is applied.
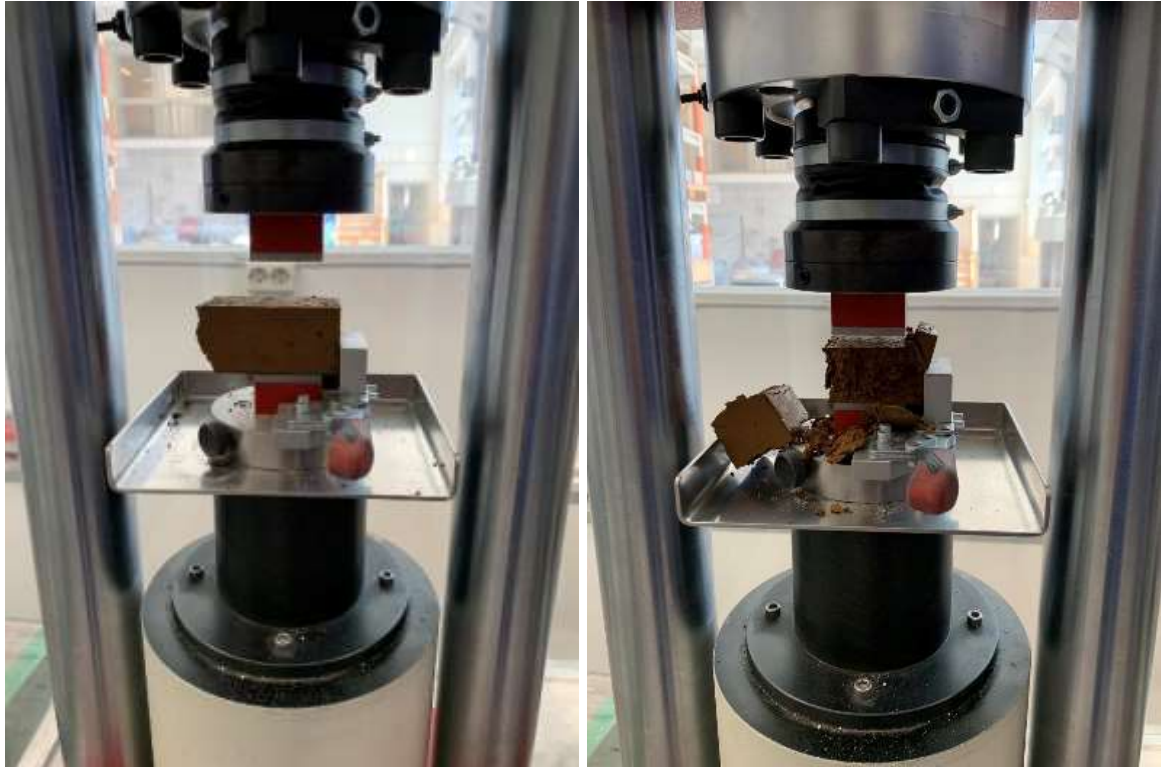
Figure 42. Local marine clay specimen during the compressive strength test. Image on the right shows the specimen before the load is applied and image on the left shows the fractured specimen after the load is applied.
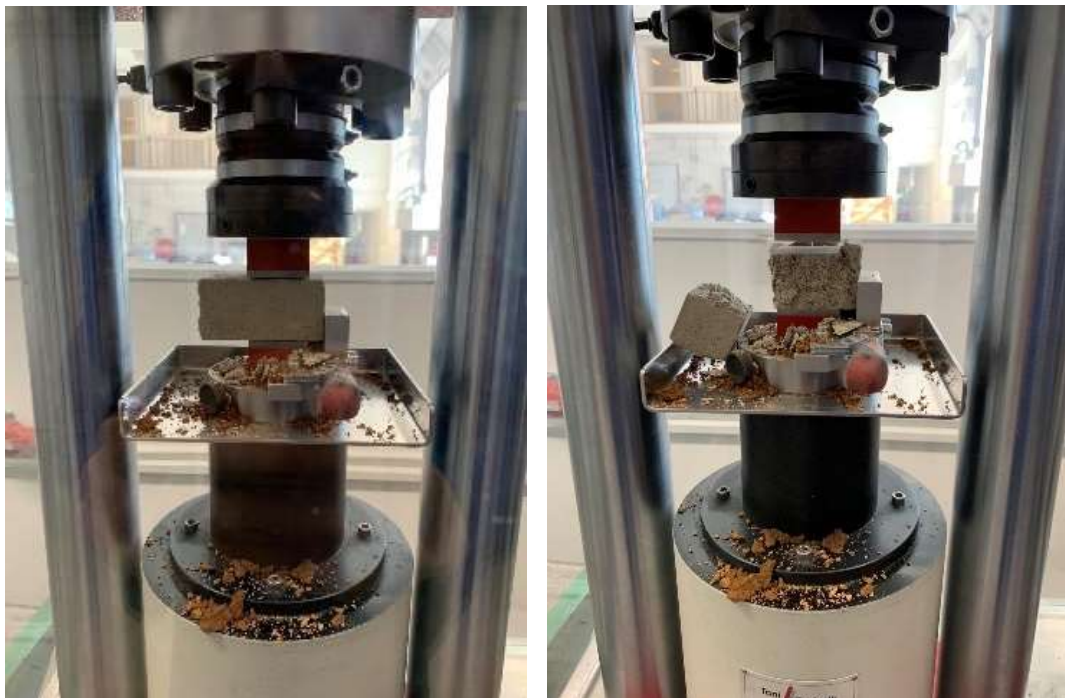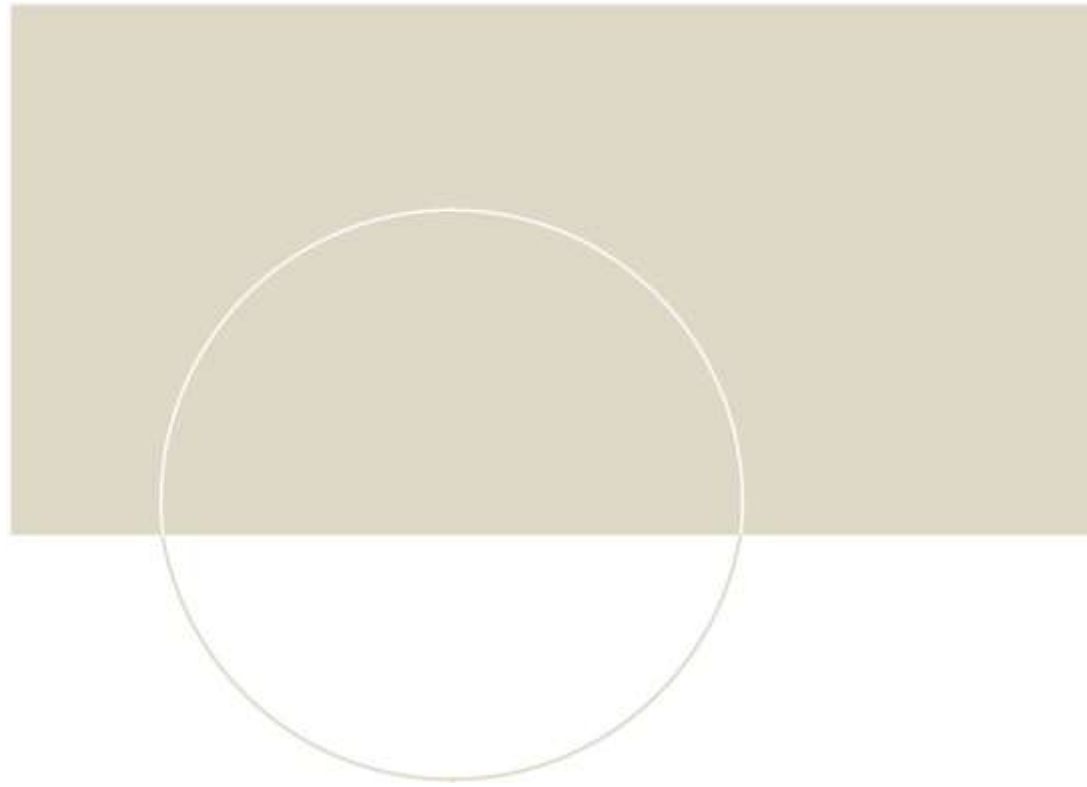

Figure 43. Pottery white clay specimen during the compressive strength test. Image on the right shows the specimen before the load is applied and image on the left shows the fractured specimen after the load is applied.