SUBLime

Sustainable Building Lime Applications via Circular Economy and Biomimetic Approaches

CERTIFICATE

This certificate is hereby awarded to:

Mert Öztürk

to certify the attendance of the
SUBLime Conference - Towards the next generation of sustainable masonry systems: Mortars, renders, plasters and other challenges
This Conference was organized by the SUBLime Consortium, from the 10th to the 12th of November 2024, and held in Funchal, Madeira.

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SUBLime

Sustainable Multiphysics Multiscale Tools for Building Lime Applications

TOWARDS THE NEXT GENERATION OF SUSTAINABLE MASONRY SYSTEMS: MORTARS, RENDERS, PLASTERS AND OTHER CHALLENGES

PROGRAMME

11-12 November 2024

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Welcome to the SUBLime Conference

Welcome to the SUBLime Conference – Towards the next generation of sustainable masonry systems: Mortars, renders, plasters and other challenges, Funchal, Madeira, November 11-12, 2024!

The SUBLime Conference is a forum to discuss, exchange ideas and gain insights into challenges, innovations and new trends in masonry. This Conference is held within the scope of the SUBLime Network, a Marie Skłodowska-Curie Action European Innovative Training Network. SUBLime (Sustainable Building Lime Applications via Circular Economy and Biomimetic Approaches) trained researchers in multiple scientific and engineering fields for a better understanding and development of sustainable innovation solutions for mortars, renders and plasters in new construction and conservation of the built heritage. This conference is a key platform for dissemination of the SUBLime's results, together with an opportunity to discuss and share research on sustainable masonry systems and other challenges.

The SUBLime Network contributes with original research in areas that have been relatively unexplored in the context of lime-based materials. These include microstructural and chemical characterization, test methods for delayed effects and durability, simulation of microstructural development, and upscaling towards meso- and macro-scales. The Network also aims to deepen understanding of fundamental mechanisms such as creep and shrinkage, and to develop new functional materials that provide self-cleaning, self-healing, or other capabilities, like accelerated hardening. Innovations are geared towards achieving carbon neutrality or even negativity, aligning with EU objectives on environmental performance.

The scientific programme of the SUBLime Conference comprises four keynote lectures from internationally renowned researchers and is structured in several thematic sessions in different fields of research. The diverse range of topics covered in these proceedings reflect the interdisciplinary nature of the field, spanning advanced material technologies, structural optimization, environmental impact assessments, and real-world applications.

More than 150 participants from more than 30 different countries joined, making the SUBLime Conference a truly international event. An exciting program includes 112 contributions concerning a wide range of activities and research fields in masonry. This conference benefits immensely from joining young researchers with more senior academics and professionals, with PhD students representing 40% of participants, foreseeing a bright future for this community.

We warmly thank the contributors, authors, reviewers, speakers and the sponsors of the event and are sure that the conference offers fruitful discussions and a pleasant time in Funchal, Madeira.

Funchal, November 2024

Paulo B. Lourenço
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Improving the strength of metakaolin-lime based binder

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Abstract. Pozzolanic reaction of low-calcium metakaolin (MK) with calcium hydroxide (CH) at ambient temperature in the presence of water forms a series of hydrated phases such as tetracalcium aluminate hydrate (C_4AH_{13}), calcium silicate hydrate (C-S-H) and calcium aluminum silicate hydrate (stratlingite - C_2ASH_8). Stratlingite is the main crystalline phase and is responsible for the strength of the binder. Tetracalcium aluminate hydrate (C_4AH_{13}) is carbonated upon contact with air or converted to hemicarboaluminate and/or monocarboaluminate if the system contains excess carbonate phases (calcite or calcareous aggregates). However, the calcium aluminate hydrates formed after the reaction of MK with lime lose their strength over time due to their instability. Especially in a high humidity environment where there is no carbonation, the presence of both stratlingite and (CH) in the binder creates weak phases called katoite ($Ca_3Al_2(SiO_4)(OH)_8$) and can reduce the mechanical strength and durability. On the other hand, it has been determined that using chemical activators to increase the pozzolanic reactivity is the most feasible method, although it increases the cost of the material. In this study, it is aimed to eliminate the phases that cause katoite formation and improve the performance of the binder by using alkaline hydroxide solution in a mixture of metakaolin and slaked lime, similar to the pore solution caused by hydrated cement. For this aim, the effect of sodium carbonate (N-Na_2CO_3), quicklime (C-CaO) and calcite (CC-$CaCO_3$) on the (CH-$Ca(OH)_2$) activated metakaolin system is investigated through the experimental campaign. The preparation of the mixtures is done by the novel one-part mixing method.

1 Introduction

In pozzolanic limes, the reactivity of the pozzolans depends on their active (colloidal) silica and alumina content, preparation (fine grinding ≤75 microns) and storage. Acidic alumina and reactive silica (SiO_2+Al_2O_3) combine with alkali hydrated lime $Ca(OH)_2$ (CH-Portlandite) at normal temperatures in the presence of moisture to form stable insoluble

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compounds [e.g., calcium alumino-silicate hydrates (C-A-S-H)] [1] with binding properties. The lesser the amount of (CH) after the reaction, the higher the reactivity or pozzolanicity of a pozzolan. Lime pozzolan mixtures have two competitive hardening mechanisms; carbonation and slow process of pozzolanic reaction (hydration). Extremely fast carbonation could inhibit slower pozzolanic reactions, reducing the cationic diffusion. Hydraulic compounds are actually produced by the pozzolanic reaction, which occurs when the material is sufficiently saturated with water to consume the free lime. Mortar with a lime/pozzolan ratio of 1:2 (by weight) is consistently stronger than mortar with a ratio of 1:4. [2] Pozzolan will act as a filler and the mortar will have poor strength if there is not enough lime in the mortar for hydration products to bind the particles and fill in the spaces. The strength of the mortar will again decrease if there is an excessive amount of lime present, since the lime cannot function as a binder and will instead stay in the free state. The ratio is usually 1:1.

A number of hydrated phases, including tetra calcium aluminate hydrate (C_4AH_{13}), calcium silicate hydrate (C-S-H), and calcium aluminum silicate hydrate (stratlingite-C_2ASH_8 or gehlenite hydrate), are formed in the presence of water as a result of the pozzolanic reaction of metakaolin (MK) with calcium hydroxide at room temperature [3]. The primary crystalline phase that was formed, stratlingite, is what gives the mortar/binder its strength. A correlation was discovered between the rate at which MK replaced lime and the rise in stratlingite content. The resulting crystalline products are essentially the consequence of the interaction between portlandite (CH) and AS_2 (Al_2O_3. $2SiO_2$). As a result, the AS_2/CH ratio and the reaction temperature are important factors. Furthermore, carbo-aluminates can be formed if carbonate is easily accessible [4]. Lime-pozzolan mortars have been found to deteriorate with time in both practical applications and laboratory studies, with the type of pozzolan employed also playing a role [5]. Reaction kinetics were observed in the lime/MK compositions over the curing period, indicating a clear correlation between the pozzolanic product content and the rate at which lime is substituted with MK [3]. Since MK contains a significant quantity of aluminum phase, the calcium aluminate hydrates that are formed after reacting with lime are unstable, which explains why the strength gradually decreases [5]. When CH is present, calcium alumina hydrates can weaken the mortar's structure and result in a reduction in strength. In a long-term setting where carbonation does not occur, the presence of both stratlingite and CH in the mortar leads to weak phases known as katoite (C_3AH_6) (hydrogarnet) ($Ca_3Al_2(SiO_4)(OH)_8$). This is particularly prevalent at MK/CH ratios for a range of 0.6 and 0.3. For MK/CH ratios lower than 0.3, lack of stratlingite prevents the formation of katoite and for MK/CH of 1.0 and above, no hydrogarnet (katoite) forms due to the absence of CH. At around 55 °C, katoite forms in MK-CH pastes in two different ways: 1) in the first days it precipitates directly from the solution and 2) at longer times via transformation of the metastable phases (stratlingite) for MK/CH of 0.38 to 2 (between 0.5 and 1.0). However, for higher MK/CH no hydrogarnet was observed even at higher temperatures possibly due to the lack of CH [6].

Incompatible phases stratlingite and CH combine to form a low silica more stable hydrogarnet [7], or katoite, after the lengthy curing period. Katoite is a compound that can lower mechanical strength and durability and has detrimental effects on matrices containing metakaolin. Consequently, katoite generation is avoided by utilizing MK at the ideal rate in an environment with high humidity. The ideal amount of MK, however, needs to be re-evaluated because, in normal atmospheric conditions, when CO_2 penetration is unrestricted, the carbonation that takes place counterbalances the consumption of portlandite in the pozzolanic process [6].

The cementation properties of pozzolanic materials require a source of lime. $Ca(OH)_2$ can be used to do this. On the other hand, in the low alkaline environment induced by calcium hydroxide, low calcium pozzolans gain strength slowly. Therefore, it may be appropriate to add an additional activator to the system to raise the pH of the system and improve early

activation. It has been found that the most efficient method to improve the pozzolanic reactivity is to use chemical activators (4% Na_2SO_4 and $CaCl_2$), but this would raise the material's cost [8]. Alkaline carbonate activators such as Na_2CO_3 provide very slow strength development in low calcium systems because they provide a low alkaline environment. On the other hand, it has been found that activation with sodium carbonate can provide good performance. The pH of sodium carbonate solution is 10-11, which is lower than slaked lime. The pH of slaked lime is 12.5. By mixing these two alkalis, the pH value of sodium carbonate can rapidly increase to 14 by the following reaction:

$$Na_2CO_3 + Ca(OH)_2 \Rightarrow 2NaOH + CaCO_3\downarrow \quad (1)$$

In this case, NaOH activation replaces sodium carbonate activation [9]. As a matter of fact, with Na_2CO_3 (CH/N:5 by molar mass) used in the strength development of fly ash with $Ca(OH)_2$, the dissolution of fly ash was accelerated with the increasing alkaline environment in the early reaction period, alumina and silica species were released and took part in the formation of calcium silicate hydrate (C-S-H), CH was rapidly consumed and $CaCO_3$ was formed, by the pozzolanic reaction between lime with fly ash C-S-H or (C-S-H(I) was formed. CH was rapidly consumed after 7 days, and 4-5 times higher compressive strength was obtained compared to samples activated only with CH. The pore-filling effect of the $CaCO_3$ content, which is formed from the initial reaction between $Ca(OH)_2$ and Na_2CO_3, is not the primary reason for the development of strength [10]. However, to have an accelerating effect by seeding the formation of C-S-H gel, which increases strength in the early period [11].

In low calcium alkali activated systems ($(Na,K)_2O$-Al_2O_3-SiO_2-H_2O system), the activated material (e.g. metakaolin) mainly contains aluminum and silica; CaO content is low. The reaction product of this system is a three-dimensional inorganic alkali polymer, i.e. a N-A-S-H (or alkali alumino silicate hydrate) gel [12]. In this type of systems, to initiate the reaction, either more aggressive curing conditions (high alkaline environment and cure temperature 60-200 °C) or the incorporation of an additional source of lime to the system is required [13]. In the presence of Ca^{+2}, both N-A-S-H and C-A-S-H gels could be observed with the replacement of Al^{3+} by Ca^{+2}. Accordingly, incorporation of appropriate contents of cheap components rich in Ca, like CaO or limestone as alkaline earth carbonate minerals, in the presence of suitable activator chemistry could decrease the cost and energy consumption (calcination of metakaolin) of the preparation of the material [14].

Finely ground limestone as a complementary cementing material can provide improved material properties through the formation of additional "carboaluminate phases" in ternary "Portland cement-metakaolin-limestone" (LC^3) blended binder systems. $CaCO_3$ supplied to the system by limestone reacts with alumina in metakaolin and lead to the formation of a phase with 'AFm' structure (Alumina (Al_2O_3)-Ferric Oxide (Fe_2O_3)-mono) and increased the solid volume ratio. Additionally, the reaction of metakaolin and limestone consumed calcium hydroxide [15]. A study on the metakaolin- 3 and 5M NaOH-$CaCO_3$ (30, 50, 70%) combination revealed similar pore solutions to those induced by hydrated cement. AFm phases were found in 3M NaOH at 20 and 80 °C, as well as in 5M NaOH at 80 °C. The acidic environment created by 3M NaOH caused the limestone to dissolve a little more, and at room temperature, a geopolymer gel primarily composed of C-A-S-H developed. The compressive strength was enhanced when MK was replaced with 30% and 50% limestone after heat treatment [16]. Similar to this, 6 and 8 mol Ca/Mg-carbonate-based industrial wastes were used as solid activators to produce metakaolin-based one-part geopolymers, with stratlingite forming as the primary crystalline phase [17].

Taking into consideration the aforementioned issues, the current study seeks to gain a deeper knowledge of the improved pozzolanic reaction by adjusting the mortar's alkalinity

using different chemicals. By employing an alkaline hydroxide solution in a mixture of metakaolin and slaked lime, which is comparable to the pore solution created by hydrated cement, the goal is to remove the phases that lead to katoite development in the mortar and to improve the mortar's performance. In order to achieve this aim, the impact of quicklime (CaO), calcite ($CaCO_3$), and sodium carbonate (Na_2CO_3)-which Türkiye possesses the second-largest reserves of in the world-on the $Ca(OH)_2$ activated metakaolin system was examined through an experimental campaign. The novel one-part mixing process is used to prepare the mixes.

2 Materials and methods

This study investigated the effects of calcium and alkali-based additives on the hydration mechanism of lime-pozzolan mortars through mechanical and physical experiments. Metakaolin (MK) was obtained as "Ground Metakaolin CALK-85 UMB" from the Kaolin Company. The chemical, mineralogical, and physical properties of the MK are given in Table 1. Its SiO_2+Al_2O_3+Fe_2O_3 content (97.54%) is higher than 70.0%, while SO_3 and Cl contents are lower than 3.0% and 0.1%, respectively. The pozzolanic activity of the metakaolin was tested according to the Turkish Tras Standard 25 (TS 25) and it fulfils the requirements of TS 25 [18] in order to be used as a pozzolan in cement, concrete, and other binder types. A pozzolanic raw material should have a minimum 1.0 MPa flexural strength and 4.0 MPa compressive strength, according to TS 25. Pozzolanic activity test results of MK (2.41 MPa and 21.15 MPa for flexural and compressive strengths respectively), revealed that it has a high pozzolanic character. According to the mineralogical analysis, MK contains 78% amorphous phase, which is an important phase to have high pozzolanic properties. The particle size distribution reveals that 99.3% of MK can pass through 45 μm sieve.

CH (hydrated calcium lime-Cl 90 S) was available in powder form with a fineness higher than 90 μm. CaO (C) (quicklime-CL 80 Q-90 μm) in compliance with the BS EN 459-1 [19] was supplied from Nuh Yapı. $CaCO_3$ (CC) with 90-99% of the particle size smaller than 2 μm was supplied from Erciyes Mikron in Türkiye. Analytical grade of N (sodium carbonate anhydrous) with a minimum 99.5% Na_2CO_3 (CAS No: 497-19-8) content supplied from Eti Soda was used as an alkaline activator.

Table 1. Chemical and mineralogical compositions of MK with particle size distribution.

Metakaolin (MK)									
Chemical composition in Oxides	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	LoI*
Weight (%)	55.50	42.04	0.70	0.23	0.11	0.15	0.66	0.10	0.30
Mineral Phases	Amorphous Phase		Quartz		Mica		Mullite		Others
Weight (%)	~78		~9		~6		~5		~2
Sieve size (μm)	45	32	20	10	5	2	1	0.5	D50
Passing (%)	99.3	98.9	97.5	91.6	78.5	53.6	36.1	20.6	1.74
*LoI is loss on ignition at 1000 ºC.									

The present investigation focused on comparing the two MK/CH ratios at 55 °C curing: 0.5 MK/CH (MK33CH), where stratlingite is unstable and katoite formation is observed and 2 MK/CH, where stratlingite persists and stable. The MK/alkali activator ratio was maintained at 2:1 (M67) and 1:2 (M33) in all mortars designed for the study. $Ca(OH)_2$ was the only activator utilized in the first stage. In the next stages, only Na_2CO_3 and Na_2CO_3+CaO or Na_2CO_3+$CaCO_3$ were added to the mortar mixtures. Na_2CO_3 was set by weight of the binder at 9 % in MK67 and 18% in MK33. That is, the molar quantities of N are 0.08 for MK67 and 0.17 for MK33 mortars. N/ (CH+N+C or CC) ratio by weight was kept constant at 0.27. The binder-to-sand ratio was kept constant as 0.3 by weight throughout the study. The workability of the fresh binder was specified with a flow table test in accordance with ASTM C593-19 [20]. The sample compositions were given in specimen codes as follows: MK: Metakaolin; 67 and 33: The ratio of MK/Activator; CH: $Ca(OH)_2$ (Calcium hydroxide); N: Na_2CO_3 (Sodium Carbonate), C: CaO (Calcium Oxide); CC: $CaCO_3$ (Calcium Carbonate).The detailed mixing ratios of the mortars are given in Table 2.

Table 2. Specimen codes and mixing ratios by weight.

Specimen Code	**MK (g)**	**CH $Ca(OH)_2$ (g)**	**N Na_2CO_3 (g)**	**C (CaO) (g)**	**CC $CaCO_3$ (g)**	**Activator : MK**	**Binder: Sand**	**Flow (%)**
MK67CH	67	33				0.5	0.3	70
MK33CH	33	67				2		
MK67CHN	67	24	9			0.5		
MK33CHN	33	49	18			2		
MK67CHNC	67	15	9	9		0.5		
MK33CHNC	33	31	18	18		2		
MK67CHNCC	67	15	9		9	0.5		
MK33CHNCC	33	31	18		18	2		
CH, N, C or CC were accepted as alkali activators (AC). N/AC ratio was kept constant as 0.27. Specific Gravity (g/cm^3): MK: 2.49; CH: 2.21; CC: 2.7; Sand: 2.65.								

MK, CH, N, C/CC, and standard sand were mixed in dry form for 5 min by hand (Fig. 1a) and then thoroughly mixed by a mortar mixing machine for another 5 min (Fig. 1b). The amount of water was arranged according to the flow table test (Fig. 1c). After mixing, tap water was gradually added to the dry binder, and mixing continued until a homogeneous fresh mortar was obtained. The fresh mortars were cast into the molds 40 mm x 40 mm x160 mm in size (Fig. 1d). Mortars were cured at 55 °C and a relative humidity of 95± 5% for 7 days in order to promote the hydration process over the carbonation reaction (Fig. 1e). They were then taken out of the molds and left to be stored for 11 days at room temperature (T=23±2 °C and RH= 95±5%) in sealed plastic bags to hinder the carbonation reaction (Fig. 1f). The specimens ready for the tests are shown in Fig. 1g.

The specimens were tested for unit weight according to the BS EN 1015-10 [21], capillary water absorption according to the BS EN 1925 [22], water absorption under atmospheric pressure according to the BS EN 13755 [23], dynamic ultrasound velocity/MoE according to the BS EN 14579 [24], flexural and compressive strengths according to the BS EN 196-1 [25].



Fig. 1. (a) Preliminary mixing of raw materials; (b) Producing mortar through a mortar mixing machine; (c) Arrangement of water quantity by flow table test; (d) Molding of the fresh mortar; (e) Curing of mortar in the oven; (f) Storing of the specimens after oven curing; (g) The specimens that were ready for the tests.

3 Results and discussion

3.1 The comparison of the properties of MK67 and MK33 mortars

3.1.1 Mechanical properties

The mortars were evaluated primarily according to the MK/AC ratio (by weight). All the mortars were cured under limited carbonation reaction. The compressive and flexural strengths of the mortars are given in Fig. 2.

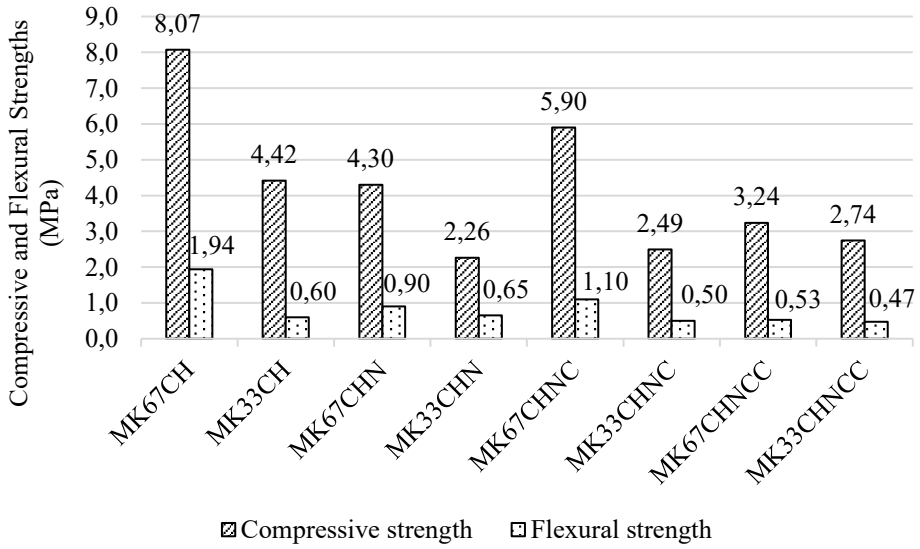


Fig. 2. Compressive and flexural strengths of the mortars.

MK67 mortars yielded generally higher ratings for compressive and flexural strength. Since MK33 mortars have activator ratio twice that of metakaolin, it is probable that alumina silicate precursor has been insufficient to produce enough C-A-S-H to provide the binder strength. Compressive strength decreasing rates differ based on the kind of activators added to the mixture:

While the compressive strengths of MK33 mortars compared to MK67 mortars decreased by 0.55, 0.52, 0.42 and 0.85-fold when CH, CHN, CHNC or CHNCC were used, respectively, the flexural strength values decreased by 0.31, 0.72 and 0.46-fold in parallel with these values. However, only the flexural strength of CHNCC increased by 1.34 times, and this mortar showed the least decrease in compressive strength with 0.85 times (Fig. 2). Compressive strength measures the maximum compressive stress a material can withstand before failure and is influenced by factors like the material's molecular structure, defects, bonding strength. This shows that M33 mortars are more prone to deformation or failure under compression than M67 mortars. Dynamic ultrasound pulse velocity measures how quickly sound waves propagate through a material. It's influenced by factors such as the material's density, elasticity, and internal structure. When CH, CHN, CHNC, or CHNCC were utilized, the ultrasound values of MK33 mortars compared to MK67 mortars revealed a 0.97, 1.20, 0.87, and 1.25-fold change, respectively (Fig. 3). In terms of the MoE values determined by ultrasonic testing, the M33 and M67 mortars performed similarly. For CH, CHN, CHNC, and CHNCC, respectively, the MoE values gave a change of 0.92, 1.50, 0.77, and 1.76-fold.

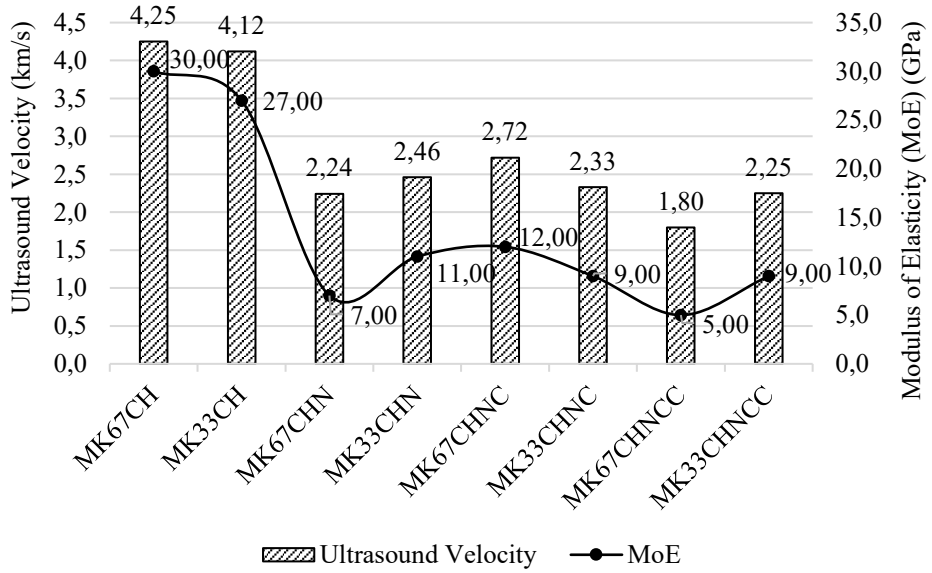


Fig. 3. Dynamic ultrasound velocity and modulus of elasticity values of the mortars.

In comparison to the other mortars produced, M67CH and M33CH exhibited MoE values that are as high as cementitious mortars. They can withstand much higher stresses before deforming significantly, making it a preferred material for structural applications where high strength and stiffness are required. Conversely, other mortars with low modulus of elasticity varying between 5-11 GPa present a plastic zone and may deform more easily under stress and are less stiff. They may have the ability to absorb a higher degree of deformation before the breakage and accommodate movement through micro-cracking.

3.1.2 Physical properties

The porosity and water absorption values of the mortar specimens are given in Fig. 4.

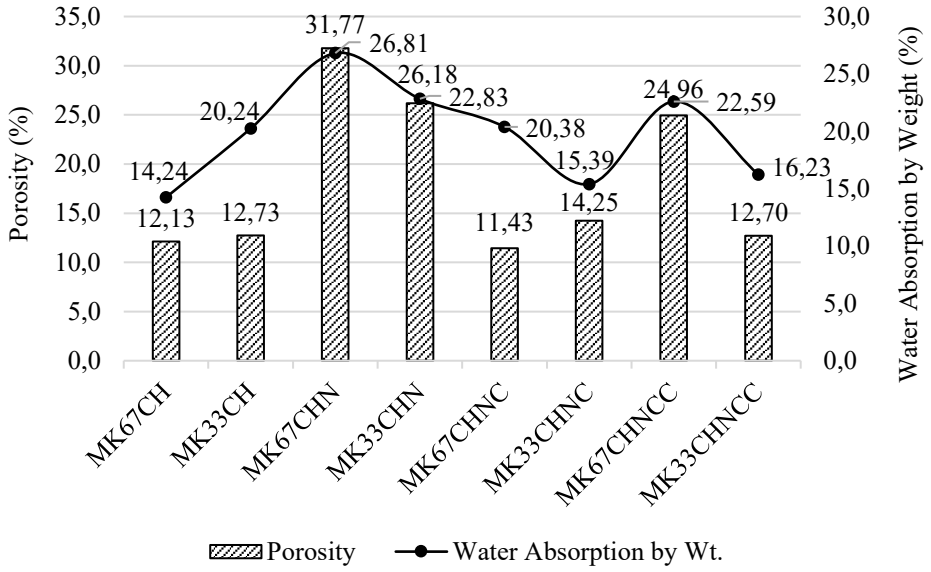


Fig. 4. Porosity and water absorption values of the mortars.

In general, there was consistency between the mortars' mechanical and physical properties. Porosity and water absorption, declined along with the increase in compressive strength. While the porosity of the MK67CH and MK33CH mortars containing solely CH stayed nearly the same, there was a 1.4-fold rise in water absorption in accordance with the weight ratio of slaked lime in the mortar. The capillary curves and capillarity coefficient values of all mortars are depicted in Fig. 5. The capillarity coefficient, which rose 2.81 times in the MK33CH mortar suggests that the mortar's capillary void ratio has increased, leading to an increase in capillary pressure (Fig. 5). Adding N to the mortar did not result in a different condition. In comparison to MK67CHN, the capillarity coefficient of MK33CHN increased by 2.92 times. Among the MK67 mortars to which sodium carbonate activator was added, MK67CHNC mortar yielded the maximum strength and had a capillarity coefficient 4.24 times lower than MK33CHNC. This implies that the capillary pressure has dropped and the pore size distribution has become finer. The capillary void ratio rose in accordance with the weight ratio of C in the mortar. Conversely, in the samples containing CC additive, the capillarity coefficient stayed rather constant throughout both MK67 and MK33 ratios. This suggests that the non-reactive limestone particles, particularly in MK33CHNCC, function as fine filler and raise the packing density.

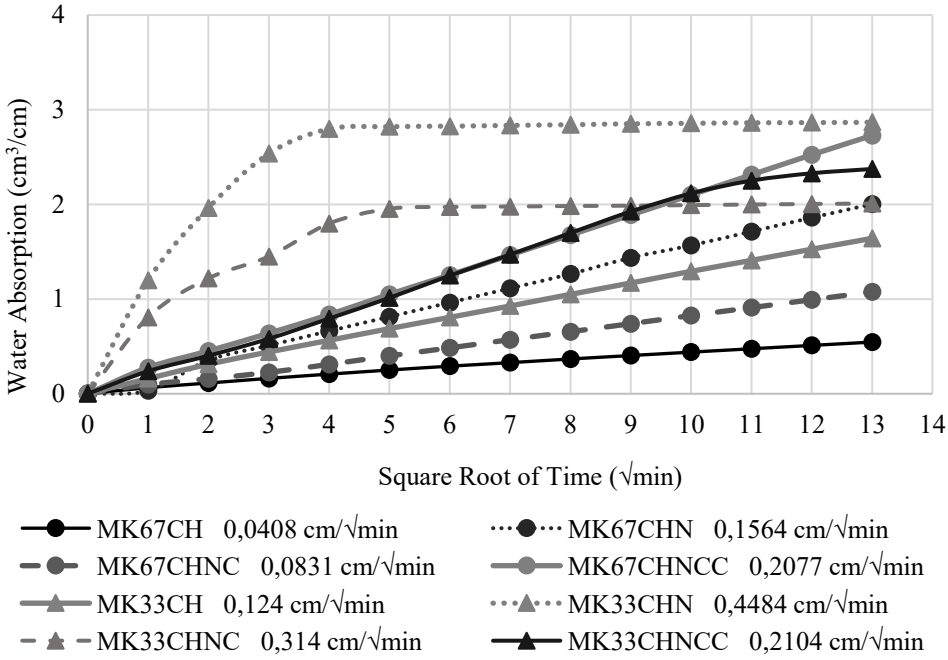


Fig. 5. Capillary curves of the mortars.

The water absorption (avg. 17%), and capillarity coefficient (avg. 0.0654 cm/min^{-2}) of MK67CH and MK67CHNC mortars are comparable to their rather low porosity values (avg. 12%). These characteristics indicate that the mortars have finer pore structure and fewer capillary voids. Blended pastes of lime and cement include two kinds of pores; capillary pores (10–0.005 μm) and the gel pores (<0.005 μm) that are associated to the C–S–H gel [26]. The MK67CHN and MK67CHNCC mortars have higher porosity (avg. 28%), water absorption (avg. 25%), and capillarity coefficient (avg. 0.1838 cm/min^{-2}) than MK67CH and MK67CHNC mortars by 2.4, 1.43, and 2.81 times, respectively. The mortars became more porous as a result of the activators (N and CC) utilized, which increased their water absorption. Moreover, the capillary void ratio increased. A higher capillarity coefficient indicates a greater ability of a material to draw liquid into its pores or interstitial spaces through capillary action.

The MK33CHN mortar has the lowest compressive strength (2.26 MPa), highest porosity (26%), water absorption (23%), and capillarity coefficient (average 0.4423 cm/min^{-2}) values among the MK33 mortars. This material has a high capillary void ratio. Capillary cracks seen in this mortar after production may have a role in the decrease of these values. In comparison to MK33CHN, the porosity, water absorption, and capillarity coefficient values of the other mortars in this group that contained sodium carbonate (N), reduced by an average of 0.51, 0.69, and 0.63 times, respectively. When calcium oxide (C) and calcite (CC) were added to mortars, the mortars were more packed and absorbed less water. Moreover, C and CC decreased the capillary void ratio. As such, these mortars had slightly higher compressive strengths than MK33CHN.

3.2 The properties of MK67 mortars

The samples of the MK67CH series produced in the study, just before the experiments, are shown in Fig. 6.

MK67CH: In the MK67CH mixture, the highest compressive strength (8.07 MPa) and flexural strength (1.94 MPa) were obtained by adding only CH as an activator (Fig. 6a). This mixture can be classified as eminently hydraulic lime mortar.

MK67CHN: Increasing the reactivity of the pozzolan and reinforcing it by forming C-A-S-H and N-A-S-H gels in the mortar's structure can help with the durability issues that vary based on the MK/lime ratio and carbonation that may occur in lime-metakaolin mortars. With this approach, in MK67CHN (Fig. 6b), sodium carbonate (N) was added to the binder so that the N/AC was 0.27 and CH/AC was 0.73 by weight. Compared to MK67CH the compressive strength decreased by 0.53 times and the flexural strength decreased by 0.46 times. According to the formula ($Na_2CO_3 + Ca(OH)_2 \Rightarrow 2NaOH + CaCO_3\downarrow$), it was expected that N and CH, which have relatively low pH, would combine to give 2NaOH, increasing the pH of the mortar to 14 and facilitating the dissolution of Si and Al ions from MK. Although this was expected to form N-A-S-H gel and additionally, C-S-H which occurs through the pozzolanic reaction between MK and lime within the material, it was understood that this transformation could not fully occur in this new structure. The N/CH molar ratio in the mixture is 0.26 and only 26% of the $Ca(OH)_2$ (by mol) was supposed to be used for the formation of $CaCO_3$, while the other 74% of the initial $Ca(OH)_2$ must have been used for C-S-H formation [10]. As a result, the N contribution was insufficient, it reduced the effect of CH by almost half and reduced the strength.

MK67CHNC: The inclusion of quicklime (CaO) into the mortar can raise the temperature of the system to approximately 60°C because of the high exothermic heat of dissolution [1]. Additionally, the aluminosilicate binder can be decomposed into reactive silica and alumina monomers, which can enhance the geopolymerization reaction and increase strength through the formation of binder phases [17]. For this aim, CaO (C) incorporated in the mortar at a rate of 0.27 of the activator weight and the CH/AC dropped from 0.73 to 0.46. The compressive and flexural strength strengths of this MK67CHNC mortar (Fig. 6c) were obtained as 5.9 MPa and 1.10 MPa, respectively and increased by 1.37 and 1.22 times compared to CHN. This mortar can be considered as eminently hydraulic lime mortar. Since the CH/AC ratio by weight (0.45) of this MK67CHNC mortar decreased by 0.63 times compared to MK67CHN, the N/CH molar ratio increased from 0.26 to 0.41 and becomes 1.60 times higher. In the initial stage of the reaction, only 41% of $Ca(OH)_2$ (in moles) should have been used for the formation of $CaCO_3$, while the other 59% of the initial $Ca(OH)_2$ should have been used for C-S-H formation. However, the mass percentage of (CH+C) in MK67CHNC mortar differed from that of CH in MK67CHN mortar. Even though the amount of CH in the mortar is decreasing, incorporating CaO (C) to the mixture, may have facilitated the reaction by dissolving metakaolin into reactive silica and alumina monomers in a relatively low alkaline medium. CaO (C) may also contribute to the pozzolanic reaction with MK when it slakes with mortar water. Furthermore, raising the N/CH molar ratio increased the pH of the medium. As a result, CaO increased the strength of the mortar by probably enabling the formation of N-A-S-H and C-A-S-H.

MK67CHNCC: In cementitious mortars, aluminum produced in the early stages of the reaction is bound to hydrocalumite-like AFm type phases and the presence of limestone promotes the release of Al and Si ions from metakaolin [16]. Instead of adding CaO (C) to the mixture at a rate of 0.27 of the activators by weight, finely ground $CaCO_3$ (CC) was added to produce MK67CHNCC mortar (Fig. 6d). 3.24 MPa and 0.35 MPa, respectively, were found as the compressive and flexural strength values. It is possible to categorize the mortar as moderately hydraulic lime mortar. The compressive and flexural strengths of this mortar decreased respectively by 0.55 and 0.32 times compared to MKCHNC.

In contrast to other mortars in the M67 mortar group, this mortar had the lowest elasticity modulus; yet, it is recognized that the material behaves brittlely under bending stresses. Actually, compared to other mortars, the ratio of its compressive to flexural strength is found

9, which is about twice as high. The N/CH molar ratio of this mortar is the same as 67MKCHNC and is 0.41. As it is known, $CaCO_3$ can dissolve at a lower rate in basic environment. It may not ensure further dissolution of MK and therefore, the reaction of MK and the addition of CC reduced the mechanical strength of the mixture of by half compared to (C).



Fig. 6. MK67 mortar specimens: (a) MK67CH; (b) MK67CHN; (c) MK67CHNC; (d) MK67CHNCC.

3.3 The properties of MK33 mortars

The samples of the MK33CH series produced in the study, just before the experiments, are shown in Fig. 7.

MK33CH: In MK33 mortars, the highest compressive strength (4.42 MPa) but relatively low flexural strength (0.60 MPa) was obtained by adding only CH as an activator (Fig. 7a). This mixture can be classified as eminently hydraulic lime mortar.

MK33CHN: The CH:AC ratio (by weight) in the MK33CHN mixture (Fig. 7b) dropped from 2 to 0.73 when N was added at a rate of 0.27. The mortar's flexural strength improved by 1.08 times, but its compressive strength declined by 0.51 times. The compressive and flexural strengths of this mortar are 2.26 MPa and 0.65 MPa, respectively. N/CH molar ratio of the mortar is 0.26 and only 26% of the $Ca(OH)_2$ (by mol) was supposed to be used for the formation of $CaCO_3$, while the other 74% of the initial $Ca(OH)_2$ must have been used for C-S-H formation. N/MK ratio by weight is 0.54, while the CH/MK is 1.47. The decrease in compressive strength compared to MK33CH may be attributed to the NaOH, which formed from the reaction between CH and N, may hardly find an adequate supply of aluminosilicate source or pozzolanic reaction between MK and CH, whose proportion in the mixture is relatively reduced, was insufficient to form C-S-H. Additionally, microcracks induced by drying shrinkage were observed in this mortar. Consequently, the addition of N to MK33CH lessened the effect of CH and reduced the mortar's strength in half. The flexural strength of the mortar increased by 1.08 times, which would suggest that the structure of this mortar is comparatively more elastic. The ultrasonic pulse velocity and MoE of this mortar had 0.59 and 0.41-fold decrease in comparison to MK33CH mortar, exhibiting a pattern consistent with the decline in compressive strength.

MK33CHNC: In MK33CHNC mortars (Fig. 7c), the compressive strength increased by 1.10 times and flexural strength fell by 0.77 times compared to MK33CHN when incorporating CaO (C) at a rate of 0.27 of the activators by weight. The addition of C, reduced the CH ratio to 0.46 from 0.73 while the N/activator ratio is kept constant as 0.27. N/CH molar ratio of the mortar increased to 0.41 and only 41% of the $Ca(OH)_2$ (by mol) was supposed to be used for the formation of $CaCO_3$, while the other 59% of the initial $Ca(OH)_2$ must have been used for C-S-H formation. The compressive and flexural strengths were obtained as 2.49 MPa and 0.50 MPa respectively. On the other hand, the (CH+C)/activator

ratio by weight is the same as the CH/activator in MK33CHN mortar. CaO (C) contribution replacing the decreasing CH in the mixture may have increased the lime ratio of the mortar and, may have further increased the temperature of the mortar when slaking in mortar water. As a matter of fact, the increase in mortar temperature due to the high exothermic heat of dissolution of unslaked CaO may be the reason for the superficial very thin cracks observed in this sample group of MK33CHNC. CaO may also aid in the dissolution of metakaolin-based aluminosilicate by decomposing it into reactive silica and alumina monomers, which in turn may enable to form N-A-S-H and C-A-S-H in mortar, comparatively low in alkalinity. Consequently, CaO had a slightly positive effect on the mechanical strength in the mortar (1.10 times), but the material gained a more brittle structure under the flexural stress by decreasing its strength 0.77 times. Ultrasound velocity and MoE of the material dropped by 0.94 and 0.81 times compared to MK33CHN.

MK33CHNCC: When finely ground $CaCO_3$ (CC) was added to MK33CHNC mortar in the same proportion as (C) (Fig. 7d), the mortar's compressive and flexural strengths were obtained 2.74 and 0.47 MP. In comparison to MK33CHN and MK33CHNC, this mortar's compressive strength increased by 1.21 and 1.10 times, respectively, and its flexural strength fell by 0.72 and 0.94 times, respectively. It can also be classified as a moderately hydraulic lime mortar class. In the stoichiometric formation of monocarboaluminate hydrate, which is responsible for the general strength and durability of the binder, especially in systems with high amounts of aluminum and carbonate ions, when there are extra calcium ions in the aqueous solution, 1 mole of metakaolin reacts with 1 mole of calcium carbonate to form 1 mole of monocarboaluminate ($A+C\bar{C}+3CH+H\text{-----}C_3A+C\bar{C}.H_{12}$) In this case, it corresponds to a 2:1 weight ratio of metakaolin to limestone [15]. The MK/CC ratio in this MK33CHNCC mortar is 1.83, and in the mortar with a low amount of MK, CC had a more favourable impact on mechanical strength than C. The interesting thing about both MK67 and MK33 mortars containing CC additives is that they achieve comparable levels of compressive and flexural strength. While the MK/CC ratio in MK33 is 1.83 and in MK67 it is 7.44, and the ratio of fine limestone in both mortars is 0.27. That is, the amount of MK in MK67 remained higher than that of powder $CaCO_3$, on the other hand, the reaction of MK with the alkaline environment consisting of N and CH contributed to a slight increase in strength. In MK33, the amount of MK decreased and $CaCO_3$, which was 0.54 of the MK by weight, provided strength by increasing the solid volume ratio in the alkaline environment consisting of N and CH. Or, unlike other mortars, it did not reduce the strength compared to M67. CC addition produced the filling effect observed in the comparable "Portland cement and low active material" mixtures by raising the effective activator/aluminosilicate ratio. Metakaolin's reactivity enhanced as a consequence as reported in Cwirzen's [16] research. One of this mortar's main advantages is that CC doesn't go through any calcination and offers roughly the same strength as CaO in the mortar. Moreover, employing a lower amount of MK in the mortar allowed for the achievement of comparable strength.



Fig. 7. MK33 mortar specimens: (a) MK33CH; (b) MK33CHN; (c) MK33CHNC; (d) MK33CHNCC.

4 Conclusions

Following conclusive remarks can be stated from the obtained results:

- The physical and mechanical tests indicated that the studied mortars are weak: low apparent densities equal to 1.57 (g/cm^3) for M67 mortars and 1.62 (g/cm^3) for M33 mortars on average, high total porosities of about 20% for M67 mortars and 16% for M33 mortars on average, tensile and compressive strengths of the mortars limited to 0.47 (MPa) and 8.07 (MPa), respectively. The structure of the M33CHNCC is the densest accompanied by its largest apparent density, reaching 1.71 g/cm^3.
- Increasing the MK/alkali activator ratio up to 67 in the binder composition improved the strength of the material.
- N (Na_2CO_3) had the same negative influence on MK67CH and MK33CH mortars and reduced the strength of the material. On the other hand, with the addition of N in MK67 mortar, a material that still maintains its integrity and has sufficient strength can be obtained. However, microcracks due to shrinkage were observed in MK33CHN mortar, meaning the matrix was weakened. As a matter of fact, it is the mortar with the lowest strength among all mortars produced in this research.
- CaO (C) addition to the MK67CHN mortar increased the strength by 1.37 times. As a matter of fact, MK67CHNC mortar has the highest mechanical strength and therefore the consistent physical properties among the N-added samples produced. Although C also had an improving role in the strength of the MK33CHNC mortar, it remained at a lower level of 1.10 times. It is important here that the MK/activator ratio is to be high.
- While adding CC to M67CHN decreased the strength by 0.75 times, adding it to MK33CHN increased it by 1.21 times. On the other hand, both MK67CHNCC and M33CHNCC exhibited comparable mechanical properties, although the metakaolin ratios of the mortars were different. In addition, the CC contribution in the MK33 ratio also played a role in improving other physical properties.
- This research gives the preliminary results. By using complementary XRD and DTA-TG analysis, more research will be done on the primary crystalline compounds that were generated in the mortars as well as the rate at which lime was consumed in the reactions.
- Utilizing low-alkalinity activators such as CH, CaO, $CaCO_3$ and Na_2CO_3 will further lower manufacturing costs, CO_2 emissions, and energy usage.
- There has to be interest in carrying out additional research to look into the durability of the novel building materials that this study suggests.

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