

# Impact of adding limestone and metakaolin powder as cement paste replacement on durability of mortar

Mostafa Amjad Hassan <sup>1,\*</sup>, Amr Ali Gamal <sup>2</sup>, Mohamed Shahat Saif <sup>2</sup>

<sup>1</sup> Department of Civil Engineering, Faculty of Engineering at MTI Modern University for Technology & Information, Cairo, Egypt

<sup>2</sup> Department of Civil Engineering, Faculty of Engineering at Shoubra, Benha University, Cairo, Egypt

\*Corresponding author

E-mail address: [mostafa.hassan@eng.mti.edu.eg](mailto:mostafa.hassan@eng.mti.edu.eg), [amr.gamaleldin@feng.bu.edu.eg](mailto:amr.gamaleldin@feng.bu.edu.eg), [mohamed.ismael@feng.bu.edu.eg](mailto:mohamed.ismael@feng.bu.edu.eg)

**Abstract:** Portland cement is crucial in global infrastructure, notably in concrete and mortar for construction. Its production, contributing 5-8% of human-made CO<sub>2</sub> emissions, poses a significant environmental challenge amplified by rising global population and housing needs. Mitigating carbon emissions per ton of concrete is essential for sustainable construction, crucially reducing the global carbon footprint. This study investigates the impact of incorporating limestone powder (LS) and metakaolin powder (MK) as a cementitious paste volume replacement on the compressive strength, permeability, and durability of cement mortar specimens. Firstly, LS was added separately with 10%, 15%, and 20% by equal volume of cement paste while, secondly MK replaced by 20% and 30% by equal volume of cement paste and finally, combined LS and MK with ratios of 10% LS with 20% MK, 15% LS with 30% MK, and 20% LS with 30% MK were used. The results showed that higher proportions of LS decrease compressive strength, with optimal performance observed at 15% LS without additional additives. Substituting 30% MK significantly enhanced compressive strength, surpassing approximately 30% improvement compared to the OPC mortar. The combination of 15% LS and 30% MK proved most effective, achieving high compressive strength with a total replacement ratio of up to 45% of cement paste volume. The sorptivity rate decreased markedly with 15% LS and 30% MK individually, and their combination demonstrated that the optimal replacement ratio was achieved with 15% LS and 30% MK.

**Keywords:** Limestone, Metakaolin, LC3, sorptivity, Durability properties.

## 1. Introduction

The construction industry globally exerts significant demand on natural resources, utilizing approximately 35-40% of raw materials, 40% of global energy production, and around 15% of available water. Additionally, it contributes approximately 35% of global carbon dioxide emissions. [1] Effective management of natural resources in construction is crucial for advancing environmental sustainability, given its substantial economic and environmental impacts. Sand and gravel, widely used as primary raw materials in construction, serve essential roles as fine and coarse aggregates in concrete, significantly influencing concrete volume and performance. [2] With increasing construction demands, there is a corresponding rise in material costs. Concrete, a longstanding construction staple, remains a dependable choice. To enhance its cost-efficiency and environmental sustainability, various minerals can partially replace cement, forming composite cement blends with diverse binding properties. Composite cements require less energy for production compared to Portland cement and offer enhanced properties, making them prevalent in construction. Both natural and artificial pozzolans, such as volcanic tuffs, volcanic glass, volcanic ash, diatomite, and heat-treated clay, are commonly used in composite cement production. [3],[4]

Researchers are focusing on alternative materials for concrete production to address the limited supply of traditional components. Substituting these materials aims to lower concrete costs without compromising quality standards. Consequently, there is a heightened emphasis on

identifying new sources of raw materials for concrete, leading to increased exploration of various substances as potential substitutes for fine aggregate or cement, serving as fillers or replacements. Fillers in concrete occupy voids between aggregates, reducing binder requirements and improving composite material characteristics when combined with cement. They are essential for optimizing particle distribution and enhancing various properties in freshly mixed concrete, as outlined by European standard EN 13139-2018. [5]. Substituting fillers for Ordinary Portland Cement (OPC) helps reduce environmental impact by decreasing cement usage. European countries commonly use limestone powder as fillers, providing economic and ecological benefits. This practice also enhances early strength by accelerating cement hydration and reducing bleeding in concrete mixes.[6] Numerous research studies have explored how fillers affect different performance aspects of concrete. Incorporating fillers can alter concrete's physical properties by increasing its density, facilitating hydration through nucleation sites, and interacting with cement constituents.[7] Research findings consistently show that fillers, regardless of their chemical makeup, play a significant role in accelerating the reaction kinetics of cementitious systems. This acceleration is known to enhance the early-age strength development of concrete. This phenomenon underscores the broader impact of fillers in improving the performance and durability characteristics of concrete structures.[8] Soroka and Setter conducted a study investigating the influence of different fillers, considering their fineness and replacement levels, on mortar properties.

Their findings revealed that mortars containing fillers exhibited greater strength compared to the control mixture. This highlights the beneficial effect of fillers in enhancing the mechanical performance of cementitious materials, emphasizing their role in optimizing concrete mix designs.[9] Including fillers in concrete reduces pore sizes and lowers permeability, thereby enhancing the durability and resistance of the concrete to water and other deleterious substances. This improvement is crucial in extending the service life of concrete structures and maintaining their performance over time[10]. Over time, concrete durability is improved through this mechanism. Studies have shown that adding C-S-H (calcium-silicate-hydrate) in cement mixes accelerates the hydration process. Research indicates that which enhances the early development of C-S-H by accelerating hydration reactions from the beginning tricalcium silicate (C<sub>3</sub>S) seeds form additional calcium silicate hydrate (C-S-H) gel act as catalysts, enhancing the hydration of C<sub>3</sub>S. This insight, as discussed by Thomas et al., underscores the role of C-S-H in optimizing cement hydration kinetics and improving concrete performance.[11] It has been determined that incorporating a small amount of (C-S-H) into cement significantly affects the timing of the primary hydration peak, reduces the induction period, and enhances early-hour hydration rates. This is attributed to the formation of additional nucleation sites during cement particle hydration. This insight highlights the role of C-S-H in modifying cement hydration dynamics, crucial for optimizing concrete performance and durability.[11] Studies carried out by Hubler et al. [12] Concrete mixes with high Portland cement content often experience cracking due to the heat generated during hydration. To mitigate these effects, supplementary cementitious materials (SCMs) like fly ash, ground granulated blast furnace slag, silica fume, metakaolin (MK), and ground scoria (GS) are utilized to enhance concrete performance. The primary benefits of using SCMs or pozzolans include improving concrete properties such as workability, durability, and strength, conserving natural resources and energy, and promoting environmental sustainability by utilizing industrial by-products. These materials play a crucial role in advancing sustainable practices in concrete construction.[13] The raw materials employed in the production of Portland cement must possess specific proportions of calcium oxides, silica, alumina, and iron oxides. These elements are essential for achieving the chemical composition necessary for the formation of cement clinker during the manufacturing process. Maintaining precise ratios of these constituents ensures the quality and performance of the resulting cement product, meeting industry standards and regulatory requirements.[14] The ideal chemical composition of clinker typically targets 64% calcium oxide (CaO), 22% silica (SiO<sub>2</sub>), 6% alumina (Al<sub>2</sub>O<sub>3</sub>), and 3% iron oxide (Fe<sub>2</sub>O<sub>3</sub>). The interplay among these oxides directly influences the properties of the clinker and its mineralogical composition. This precise balance is crucial for achieving desired cement characteristics, including strength, setting time, and durability, reflecting the importance of chemical control in cement manufacturing processes.[15] Egypt benefits from diverse deposits of

limestone and clay spanning various geological periods. Carbonate formations, typically found in extensive plateaus along the Nile Valley from Aswan to Cairo, are prominent features in the region's geological landscape. These natural resources provide abundant raw materials essential for cement production, highlighting their strategic importance in Egypt's construction and infrastructure sectors.[15] The objective of this study is to investigate several aspects: Firstly, to assess how different methods of metakaolin (MK) replacement — both as a substitute for cement and as a replacement in paste — influence the mechanical, microstructural, and fluid transport properties of high-strength concrete made with Portland limestone cement, under varying stress-to-strength ratios. Secondly, to compare and analyze the outcomes obtained across different experimental groups. Lastly, to examine the impact of a higher limestone content (15%) on the properties of high-strength concrete. These investigations aim to provide insights into optimizing concrete mixtures for enhanced performance and durability in construction applications.

## 2. Used Materials

Ordinary Portland cement, CEM I-52.5N which follows EN 197/1. The cement, metakaolin and limestone chemical and physical properties are given in Table 1. Natural sand with a fineness modulus of 2.75 complying with ASTM C778-80 and specific gravity of 2.60 complies with ASTM C33. The particle size distributions of the limestone and metakaolin powders are shown in Figure 1 and Figure 2, respectively. The specific gravity of the used limestone powder is 2.65, while that of the metakaolin powder is 2.55. X-ray diffraction (XRD) patterns for the limestone and metakaolin powders passing sieve No. 45 are presented in Figure 3 and Figure 4, respectively. High range water reducing admixtures were necessary for mixes due to the low water/binder ratio. MasterGlenium 123 as a polycarboxylates superplasticizer with a density of 1085 kg/m<sup>3</sup> was used to achieve the appropriate consistency.

**Table 1.** Chemical and Physical Properties of Cement, Limestone Powder, and Metakaolin Powder.

<b>SiO<sub>2</sub></b>	21.20	0.64	57.1
<b>AL<sub>2</sub>O<sub>3</sub></b>	5.50	-	26.25
<b>Fe<sub>2</sub>O<sub>3</sub></b>	3.20	0.11	2.60
<b>CaO</b>	63.4	94.21	1.65
<b>MgO</b>	0.70	0.04	-
<b>SO<sub>3</sub></b>	2.40	-	-
<b>Na<sub>2</sub>O</b>	0.10	-	-
<b>K<sub>2</sub>O</b>	0.50	0.02	-
<b>loss on ignition</b>	3.00	2.15	1.65
<b>Color Powder</b>	Gray	Light Gray	Dark gray
<b>Grain Size</b>	90 µm	10 µm	10 µm
<b>Specific Gravity</b>	3.15	2.65	2.55
<b>Bulk Density (t/m<sup>3</sup>)</b>	1.51	-	-

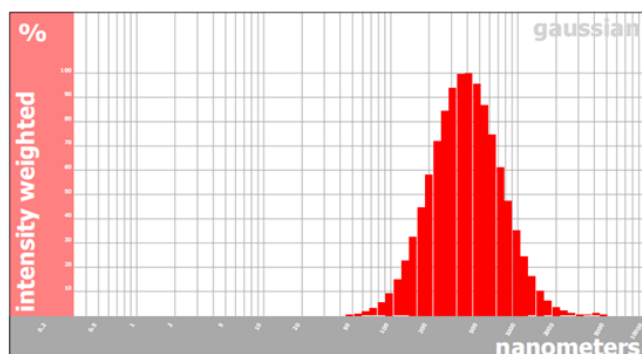


Figure 1. Limestone powder Particle size distribution.

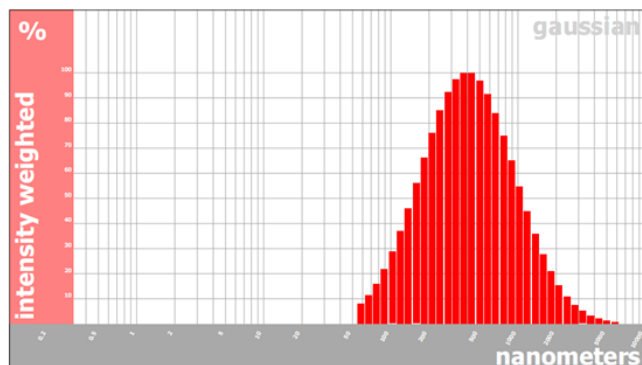


Figure 2. Metakaolin powder Particle size distribution.

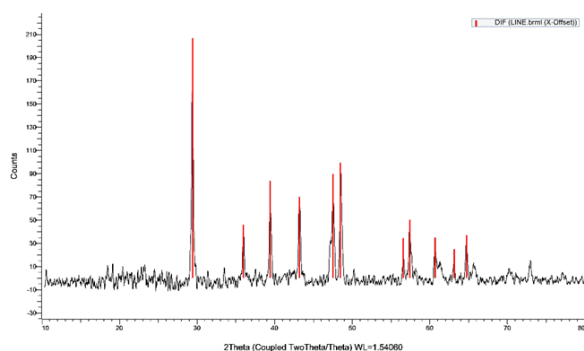


Figure 3. Limestone X-ray diffraction patterns.

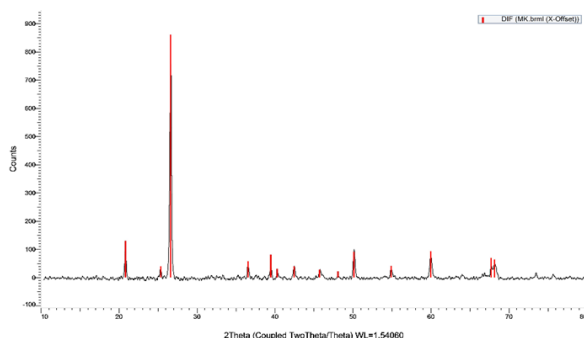


Figure 4. Metakaolin X-ray diffraction patterns.

### 3. Experimental Study

#### 3.1 Mixture Proportion

Total 9 mortar mixes were conducted for testing as indicated in Table 2. Each mortar mix was assigned x-y code in which x denoted limestone powder (LS) replacement level

and y denoted MK replacement ratio. LS ratio used by 10, 15 and 20% by weight of cement content ( $450 \text{ kg/m}^3$ ) of control mix L0/MK0, while metakaolin ratio was incorporated by 20 and 30%. The weight of both LS and MK were converted to volume and this volume was replaced by cement paste volume (volume of water + cement). In all mortar mixes, the powder paste volume was fixed at  $0.368 \text{ m}^3$ , sand content  $1620 \text{ kg/m}^3$  and w/c ratio 0.5. The cement paste volume was reduced by incorporation of LS and/or MK. Hence LS and MK were added as cement paste volume not as cement replacement. These combinations of LS and MK were carefully selected to explore the synergistic influence of both materials on the mechanical, microstructural, and durability characteristics of the concrete. The replacement strategy aimed to optimize the performance of high-strength concrete while reducing cement content, thus promoting sustainability in construction practices. all mixes as shown in table 2.

For mortar mixes, the mixing procedure adhered to the guidelines outlined in ASTM C305-82. Mortar specimens were prepared using  $50 \times 50 \times 50 \text{ mm}$  cubes, following the specifications detailed in ASTM C109-99. Curing of the mortar was performed in accordance with BS 1881: Part 111: 1983. After casting, the specimens were covered with plastic sheets for 24 hours to facilitate de-molding. Subsequently, all specimens were submerged in water at standard curing temperatures for 28, 90, 120, and 180 days, respectively. The mortar specimens were immersed in a 10% sodium sulfate solution for 90 and 180 days, respectively. Hardened and durable properties of the mixes were measured at these intervals, as illustrated in Figure 5. The experimental testing program followed in this study is outlined in Figure 5.

#### 3.2 Methods of Experimental Tests

##### 3.2.1 Compressive strength

A compressive testing machine with a maximum capacity of 2000 kN was utilized to evaluate the compressive strength of mortar specimens. The specimens, with dimensions of  $50 \times 50 \times 50 \text{ mm}$ , were carefully prepared and tested to measure their compressive strength. The testing was conducted under standardized curing conditions, maintaining a constant temperature of  $20^\circ\text{C}$  to ensure accuracy and consistency in the results. The compressive strength of the mortar was assessed at multiple curing intervals, specifically at 28, 56, 90, 150, and 180 days. This extended testing period provided a comprehensive understanding of the strength development and performance of the mortar over time, offering valuable insights into its mechanical properties and durability.

##### 3.2.2 Durability Testing.

###### Water– Sorptivity Test

The primary objective of this test was to evaluate the rate of water absorption (sorptivity) through the surface of concrete specimens. The samples were initially oven-dried at  $100^\circ\text{C}$  until a constant weight was achieved, ensuring uniformity across all specimens. Water absorption was then assessed in accordance with ASTM C1585-11. The test involved placing the specimens on a support device

positioned at the bottom of a pan, with the water level maintained at 2 mm above the top of the support device. This setup allowed for precise measurement of water uptake, providing valuable data on the permeability characteristics of the concrete.

### 3.2.3 Sulfate Resistance

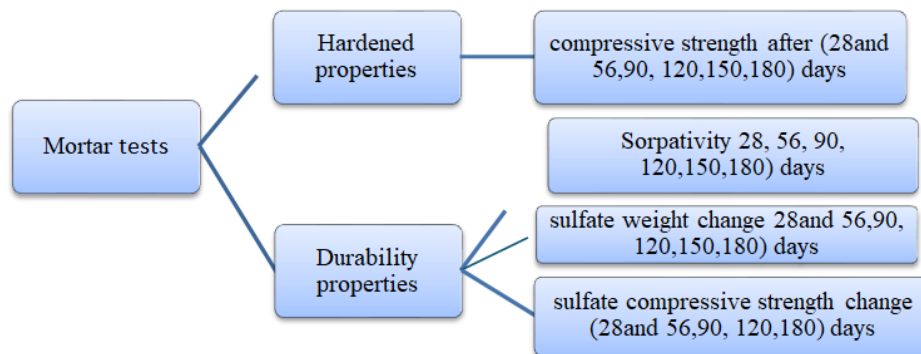
To evaluate the sulfate resistance of each mix, the compressive strength of the mortar was tested at five distinct

intervals: 28, 56, 90, 150, and 180 days. The specimens were immersed in a 10% sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) solution for a total duration of 180 days to simulate sulfate exposure. This method ensured a thorough assessment of the mortar's ability to withstand sulfate attack over time, allowing for the analysis of its mechanical performance and durability under aggressive environmental conditions.

**Table 2.** Mix Proportions of Mortar Specimens with Partial Cement Paste Replacement

Code	Water	Cement	LS	MK	Binder	W/C	W/B
L0/MK0	225	450	0	0	450	0.5	0.50
L10/MK0	215	429	45	0	474	0.5	0.45
L15/MK0	209	419	68	0	486	0.5	0.43
L20/MK0	204	408	90	0	498	0.5	0.41
L0/MK20	203	407	0	90	497	0.5	0.37
L0/MK30	193	386	0	135	520	0.5	0.37
L10/MK20	193	386	45	90	521	0.5	0.32
L15/MK30	177	354	68	135	557	0.5	0.31
L20/MK30	173	346	86	135	566	0.5	0.24

Note: All values are expressed in  $\text{kg/m}^3$  except water-to-binder ratio (W/B) which are given as ratios



**Figure 5:** Schematic Overview of the Experimental Testing Program for Cement Mortar.

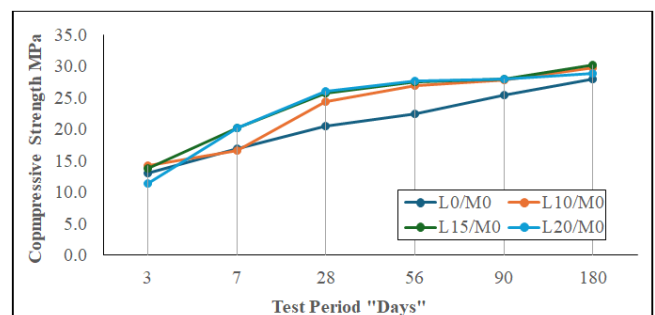
## 4. Results and Discussion

### 4.1 Compression Strength

The compressive strength results of mixes with varying limestone powder (LS) content are shown in Figure 6. The data tracks compressive strength development over a 180-day period for concrete samples with varying limestone content (0%, 10%, 15%, and 20%).

The data reveals that all mortar mixtures, including the control (L0/M0) and those with partial cement replacement by limestone (L10/M0, L15/M0, and L20/M0), demonstrate progressive strength gain over the 180-day testing period. Interestingly, the limestone-containing mortars (particularly L15/M0 and L20/M0) show accelerated early strength development compared to the control sample, achieving higher compressive strengths at 7 and 28 days. This phenomenon aligns with previous research by Bonavetti et al. (2003), who documented the "filler effect" of limestone particles, which can enhance cement hydration at early ages by providing additional nucleation sites. By the 56-day mark, all limestone-containing samples exhibit comparable

or slightly higher strengths than the control, with values ranging between approximately 25-27 MPa. This suggests that limestone replacement up to 20% by volume does not negatively impact medium-term strength development, supporting findings by De Weerd et al. (2011) regarding the compatibility of limestone with portland cement systems.



**Figure 6:** The effect of LS content on compressive strength at different age.

At later ages (90-180 days), the strength differences between all mixtures become minimal, with final compressive strengths converging around 27-30 MPa. The



L15/M0 sample ultimately achieves the highest 180-day strength, slightly outperforming both the control and other limestone-containing samples. This long-term performance contradicts some earlier concerns about potential strength reductions with higher limestone contents and supports more recent research by Bentz et al. (2017), who demonstrated that optimized limestone content can enhance both early and long-term mechanical properties through improved particle packing and modified hydration kinetics. The data presented here provides evidence that limestone replacement of cement (by volume) can be implemented up to 20% without compromising mechanical performance, offering potential environmental and economic benefits through reduced cement consumption.

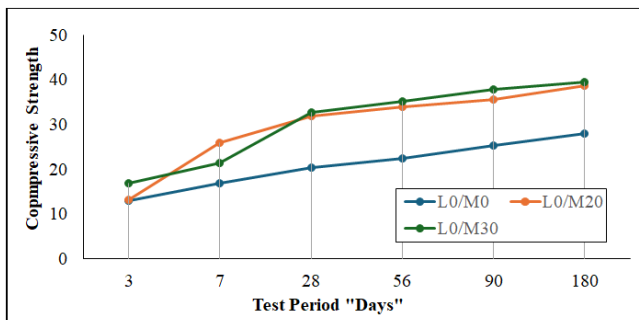


Figure 7: effect of MK content on compressive strength at different age.

Fig.7 presents a compelling comparison of compressive strength development between control mortar (L0/M0) and mortars containing metakaolin replacement (L0/M20 and L0/M30). Metakaolin-containing mortars demonstrate significantly enhanced strength performance compared to the control sample across all testing ages. At early ages (3-7 days), the L0/M30 sample shows slightly higher initial strength than L0/M20, achieving approximately 17 MPa at 3 days compared to 13 MPa for L0/M20 and 12 MPa for the control. This early-age strength advantage aligns with research by Wild et al. (1996), who documented metakaolin's ability to accelerate cement hydration through its high surface area and pozzolanic reactivity. By 28 days, metakaolin mortars reach substantially higher strengths (approximately 32 MPa) compared to the control mortar (20 MPa), representing a strength increase of about 60%. This remarkable enhancement can be attributed to metakaolin's pozzolanic reaction with calcium hydroxide produced during cement hydration, forming additional calcium silicate hydrate (C-S-H) and other binding phases that contribute to strength development, as demonstrated by Sabir et al. (2001).

The long-term strength data (56-180 days) reveals continued strength gains for all samples, with both metakaolin mortars maintaining their significant performance advantage over the control. By 180 days, the L0/M20 and L0/M30 samples reach impressive compressive strengths of approximately 39 MPa and 40 MPa respectively, compared to only 28 MPa for the control mortar—a difference of nearly 40%. The convergence of strength values between the L0/M20 and L0/M30 samples at later ages suggests that while the higher metakaolin content in L0/M30 provides some additional benefit, the optimal

replacement level may be around 20-30% by volume. This finding is consistent with research by Poon et al. (2006), who identified an optimal metakaolin replacement range beyond which diminishing returns occur due to dilution effects and insufficient calcium hydroxide for complete pozzolanic reaction. The exceptional performance of metakaolin-modified mortars demonstrated in this study supports its use as a highly effective supplementary cementitious material, capable of significantly enhancing both mechanical properties and potentially improving durability aspects as documented by Khatib and Wild (1998).

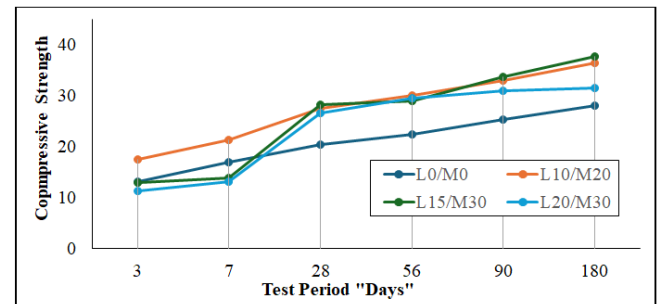


Figure 8: effect of both LS and MK content on compressive strength at different age.

Fig.8 presents a comprehensive comparison of ternary blended mortars containing varying proportions of LS and MK. At early ages (3-7 days), the L10/M20 mixture demonstrates remarkably accelerated strength development, achieving approximately 17 MPa at 3 days and 21 MPa at 7 days—significantly outperforming both the control and other ternary blends. This enhanced early-age performance can be attributed to the synergistic interaction between LS and MK, where LS particles provide nucleation sites that accelerate cement hydration while MK high surface area and alumina content promote rapid pozzolanic reactions. As Antoni et al. (2012) explained in their research, the presence of LS in ternary blends can stabilize ettringite and form carboaluminate phases through reactions with the alumina from MK, contributing to enhanced early strength development. The L15/M30 and L20/M30 mixtures, while starting with lower 3-day strengths similar to the control, show accelerated strength gain between 7-28 days, suggesting a delayed but potent synergistic effect at higher replacement levels.

By the 28-day mark, all ternary blended mortars substantially outperform the control sample, with compressive strengths reaching approximately 27-28 MPa compared to 20 MPa for the control—a remarkable 35-40% increase. This medium-term performance advantage aligns with findings by De Weerd et al. (2011), who demonstrated that LS-MK-cement systems benefit from both physical (improved particle packing) and chemical synergies (formation of additional binding phases). Between 28 and 90 days, the strength development curves show different behaviors: L10/M20 and L15/M30 continue steady strength gains, while L20/M30 exhibits a more modest rate of strength increase. This pattern suggests that at the highest LS content (20%), there may be limitations to long-term

strength development due to the dilution of reactive cement components, as previously observed by Vance et al. (2013) in their investigation of LS-MK-cement systems. Nevertheless, all ternary blends maintain their significant performance advantage over the control mixture throughout this period.

The long-term results (90-180 days) reveal particularly interesting trends within the ternary blends. The L15/M30 mixture ultimately achieves the highest 180-day strength at approximately 38 MPa, closely followed by L10/M20 at 36 MPa, while L20/M30 plateaus around 31 MPa. This divergence indicates an optimal compositional range for ternary LS-MK-cement blends, where sufficient cement remains to produce calcium hydroxide for complete pozzolanic reactions with MK, while LS content is optimized to enhance both physical packing and form supplementary binding phases. Lothenbach et al. (2008) documented similar behavior in their thermodynamic modeling of LS-supplemented cementitious systems, noting that excessive LS content can limit the formation of certain hydration products. The superior performance of the L15/M30 blend demonstrates that carefully optimized ternary mixtures can achieve significantly enhanced mechanical properties compared to unblended cement, potentially offering substantial environmental and economic benefits through reduced clinker factors while maintaining or improving engineering performance.

#### 4.2 Compressive Strength of Mortar Specimens Exposed to Sulfate Attack

The variation in compressive strength due to exposure to sodium sulfate solution over time is depicted in Figure 9. illustrates the temporal evolution of compressive strength in mortar samples with varying LS replacement levels when exposed to sodium sulfate solution. The control sample (L0/M0) exhibits a consistent decline in compressive strength from approximately 25 MPa at 28 days to 18 MPa at 180 days, indicating progressive deterioration due to sulfate attack. In contrast, the samples containing LS replacements demonstrate enhanced sulfate resistance, with the L15/M0 sample (15% LS replacement) maintaining the highest compressive strength throughout the test period. This optimal performance at 15% replacement aligns with the concept of the "dilution effect" and "nucleation effect" described by Lothenbach et al. (2008), where moderate LS additions can refine the pore structure while simultaneously reducing the amount of reactive aluminate phases that participate in expansive ettringite formation during sulfate attack.

Although all mixes incorporating LS showed improved sulfate resistance compared to the control mix, the 15% replacement level demonstrated the best performance. This suggests that moderate LS addition enhances durability, while higher replacement levels may lead to performance reductions due to excessive dilution of cementitious components. This observation corresponds with findings by Skaropoulou et al. (2013), who reported that LS additions between 10-15% can enhance the durability of cementitious systems exposed to sulfate environments by modifying the

hydration products and pore structure. The slight performance decline observed in the L20/M0 sample compared to L15/M0 suggests that exceeding the optimal replacement threshold may reduce the availability of necessary calcium silicate hydrates for strength development, as noted by Irassar (2009) in studies of LS-blended cements in aggressive environments.

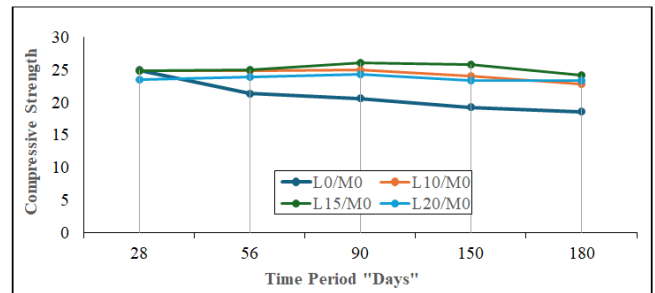


Figure 9: Effect of Limestone Powder Content on Compressive Strength Under Sulfate Exposure.

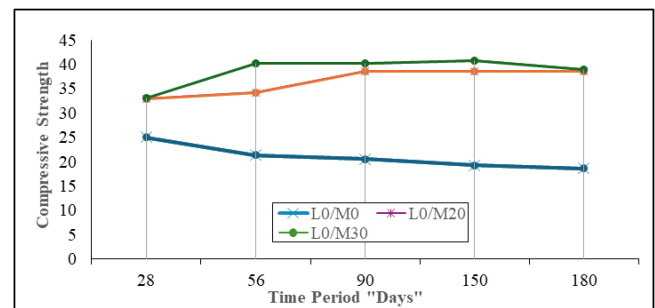
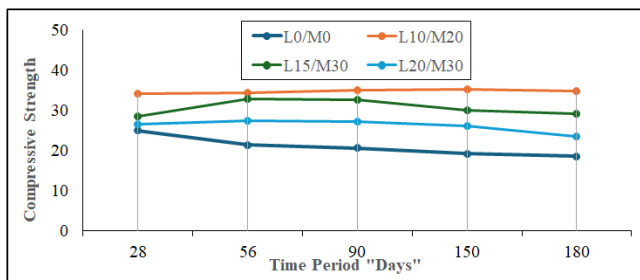


Figure 10. Effect of Metakaolin Powder Content on Compressive Strength Under Sulfate Exposure.

Fig.10 indicates that control mix exhibits the classic deterioration pattern associated with sulfate attack, declining steadily from approximately 25 MPa at 28 days to 18 MPa at 180 days, representing a 28% strength loss. In marked contrast, both MK-containing mortars not only withstand sulfate attacks but also demonstrate moderate improvement in performance compared to the control. The L0/M20 sample (20% MK) shows an impressive strength development from 32 MPa at 28 days to a peak of approximately 39 MPa at 90-150 days, maintaining 38 MPa at 180 days. Even more remarkable is the L0/M30 sample (30% MK), which achieves the highest performance, rapidly increasing from 33 MPa at 28 days to 40 MPa by 56 days and sustaining this enhanced strength throughout the test period with minimal degradation.

The superior sulfate resistance of MK-modified mortars can be attributed to several complementary mechanisms. As demonstrated by Khatib and Wild (1998), MK high pozzolanic reactivity consumes calcium hydroxide (portlandite) from cement hydration to form additional calcium silicate hydrates and aluminosilicate phases, significantly reducing the amount of portlandite available to form expansive gypsum during sulfate attack. The refined pore structure resulting from these additional hydration products decreases permeability, as documented by Courard et al. (2003), thereby limiting sulfate ion penetration into the matrix. Furthermore, Siddique and Klaus (2009) established

that MK modifications to the aluminate phase chemistry—particularly the conversion of monosulfate to more stable phases—inhibit the formation of destructive ettringite crystals that typically cause expansion and cracking in conventional mortars exposed to sulfate environments. The observed optimal performance at 30% MK replacement aligns with findings by Al-Akhras (2006), who reported that MK replacements in the 25-30% range offer optimal sulfate resistance due to the balance between pozzolanic activity and physical packing effects. Interestingly, the strength gain exhibited by both metakaolin samples between 28 and 56 days, contrary to the control's decline suggests ongoing pozzolanic reactions that continue to densify the microstructure even under aggressive exposure conditions. This phenomenon was similarly reported by Vejmelková et al. (2012), who observed continued strength development in metakaolin-blended materials exposed to sulfate solutions, attributed to the formation of additional binding phases that outpace any degradation mechanisms. The slight performance advantage of 30% over 20% replacement further supports Santhanam et al. (2003) conclusion that higher levels of high-quality pozzolanic materials like metakaolin provide enhanced long-term protection against chemical attack through multiple protective mechanisms working synergistically.



**Figure 11.** Effect of Limestone and Metakaolin Powder Content on Compressive Strength Under Sulfate Exposure.

Fig.11 illustrates the synergistic effects of LS and MK as partial cement replacements in mortars exposed to sodium sulfate solutions over 180 days. The control sample (L0/M0) exhibits the typical deterioration pattern associated with sulfate attack, declining from approximately 25 MPa at 28 days to 18 MPa at 180 days (28% strength reduction). In striking contrast, all blended systems demonstrate significantly enhanced performance, with the L10/M20 combination (10% LS, 20% MK) showing remarkable stability and the highest overall strength, maintaining approximately 35 MPa throughout the exposure period. The L15/M30 sample shows an initial strength increase from 28 to 56 days followed by minimal deterioration, while the L20/M30 sample, though still outperforming the control, exhibits a moderate strength decrease after 150 days of exposure, suggesting a threshold effect when limestone content exceeds 15% even with high metakaolin content.

MK contributes through its pozzolanic activity, consuming calcium hydroxide to form additional calcium aluminate silicate hydrates while reducing the aluminate phases available for ettringite formation. LS, as demonstrated by Lothenbach et al. (2008), stabilizes

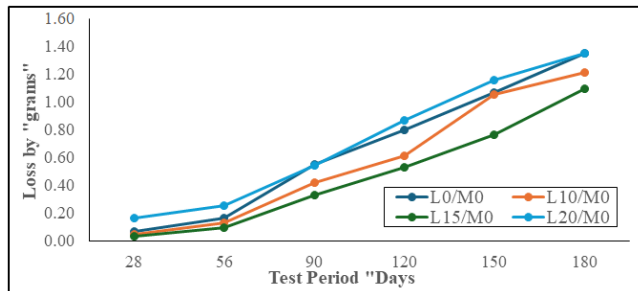
monocarbonate phases and inhibits the conversion to monosulfate that typically precedes destructive ettringite formation during sulfate attack. The observed optimal performance of the L10/M20 blend aligns with findings by De Weerd et al. (2011), who identified that moderate LS content (8-12%) combined with pozzolanic materials creates a more refined pore structure while promoting the formation of carboaluminate phases that resist sulfate deterioration. The slight underperformance of samples with higher LS content (L20/M30) supports Bentz et al.'s (2017) observation that excessive LS can dilute the binding capacity of the system when not balanced with sufficient reactive pozzolanic material. The long-term stability of the L10/M20 and L15/M30 blends over 180 days of aggressive exposure demonstrates the practical significance of carefully optimized ternary blends in sulfate environments. As noted by Shamaa et al. (2016), the superior durability of such systems stems from both chemical and physical enhancements: metakaolin's aluminum content promotes the formation of alumina ferrite monosulfate (AFm) phases, which refer to phases, a family of hydrated calcium aluminate compounds commonly found in cementitious systems. phases that incorporate carbonate ions from LS to form stable carboaluminate hydrates, while simultaneously densifying the microstructure through additional C-S-H formation. This synergistic interaction creates a system that not only resists initial sulfate ingress but also maintains structural integrity during prolonged exposure—explaining why the blended systems in the graph maintain relatively stable strength profiles while the control deteriorates progressively.

#### 4.3 Weight Loss of Mortar Specimens Exposed to Sulfate Attack

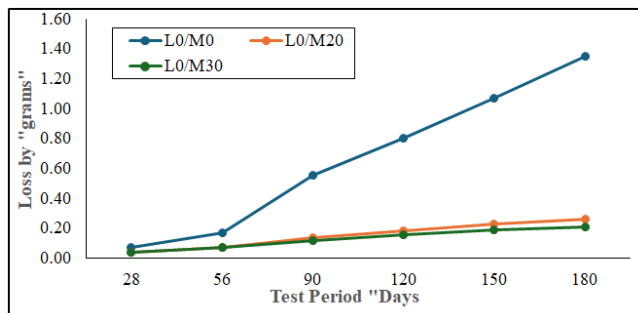
The impact of LS incorporation on weight change due to sulfate exposure is shown in Figure12, revealing a compelling pattern of sulfate resistance among mortar specimens with varying LS replacement levels. The 15% LS replacement (L15/M0) exhibits superior performance throughout the 180-day exposure period, maintaining the lowest weight loss percentage (1.10% at test conclusion) compared to other specimens. Initially, all specimens show minimal weight changes, but as exposure time increases, performance differentiation becomes more pronounced. Notably, the control specimen (L0/M0) and the 20% LS specimen (L20/M0) demonstrate similar final weight losses (1.35%), despite L20/M0 showing more rapid early deterioration. This pattern suggests an optimal LS replacement threshold exists, beyond which additional LS no longer improves and may potentially compromise sulfate resistance. The 10% LS specimen (L10/M0) maintains an intermediate position (1.21% final loss), suggesting a positive but not optimal effect at this replacement level.

This observed behavior aligns with findings from previous research on LS-blended cement. Irassar et al. (2010) demonstrated that moderate LS additions (10-15%) can enhance sulfate resistance by promoting the formation of monocarboaluminate phases that compete with ettringite formation during sulfate attack. Similarly, Schmidt et al.

(2009) found that optimal LS content creates a more refined pore structure that reduces ionic transport. However, as noted by Lothenbach et al. (2011), excessive limestone content (>15%) can dilute the cementitious matrix and increase permeability, explaining the poorer performance of the 20% replacement specimen. The observed threshold effect corresponds with Skaropoulou et al. (2013), who identified a critical LS content range of 12-15% that optimizes the balance between beneficial carboaluminate formation and detrimental matrix dilution effects in sulfate environments.



**Figure 12.** Weight Loss of LS-Based Mortar Specimens Due to Sulfate Exposure at Different Ages.

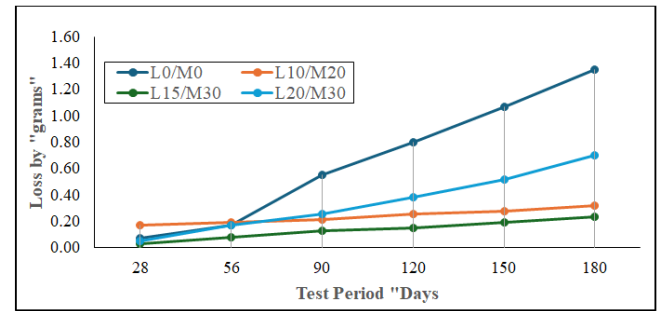


**Figure 13.** Weight Loss of MK-Based Mortar Specimens Due to Sulfate Exposure at Different Ages.

While the control sample (L0/M0) exhibits substantial deterioration with weight loss reaching 1.35% after 180 days of immersion, both MK-containing specimens show dramatically improved performance. The 20% MK replacement (L0/M20) limits weight loss to merely 0.26%, while the 30% replacement (L0/M30) performs marginally better at 0.21% after the full test period. As shown in Fig. 11. This stark contrast becomes increasingly pronounced after 56 days of exposure, where the control specimen begins accelerated deterioration while both metakaolin specimens maintain minimal weight loss trajectories. The performance gap between the 20% and 30% metakaolin replacements remains relatively small, suggesting that a 20% replacement may represent a near-optimal threshold for sulfate resistance enhancement, with only minimal additional benefit from higher replacement levels.

This exceptional performance of MK-blended mortars aligns with established research on pozzolanic materials in sulfate environments. Khatib and Wild (1998) demonstrated that MK high reactivity consumes calcium hydroxide through pozzolanic reactions, thereby eliminating a primary reactant in sulfate attack mechanisms. Additionally, Courard et al. (2003) established that metakaolin refines the pore structure and significantly reduces permeability, limiting

sulfate ion penetration. The superior performance of both MK mixes compared to the control can also be explained by Al-Akhras' (2006) findings that MK fundamentally alters the cement hydration products, producing additional calcium silicate hydrates while reducing the formation of expansive ettringite during sulfate exposure. As noted by Siddique and Klaus (2009), these combined mechanisms result in metakaolin creating a dense, impermeable microstructure that provides long-term durability in aggressive environments, explaining the consistently low weight loss observed throughout the 180-day testing period.



**Figure 14.** Weight Loss of LS and MK -Based Mortar Specimens Due to Sulfate Exposure at Different Ages.

Fig.14 reveals a complex relationship between cement replacement levels and sulfate resistance in mortar specimens. While the control specimen (L0/M0) exhibits substantial deterioration with weight loss reaching 1.35% after 180 days, all blended specimens demonstrate enhanced performance, though with varying degrees of effectiveness. The L15/M30 mixture (15% LS, 30% MK) demonstrates superior performance with only 0.24% weight loss after 180 days, followed by L10/M20 at 0.32%. Interestingly, the L20/M30 specimen shows an intermediate performance (0.70% weight loss), suggesting that increasing LS content beyond 15% may counteract some beneficial effects when combined with high MK content. This non-linear relationship indicates an optimal composition threshold exists, beyond which additional supplementary materials provide diminishing or even negative returns to sulfate resistance. The exceptional performance of the L15/M30 blend can be attributed to complementary mechanisms between limestone and metakaolin at these specific proportions. As described by Fernandez et al. (2012), limestone contributes to improved sulfate resistance through the formation of carboaluminate phases that stabilize the aluminate phases, preventing their reaction with sulfates to form expansive ettringite. Concurrently, MK high pozzolanic activity depletes calcium hydroxide through secondary C-S-H formation, as demonstrated by Kadri et al. (2011), eliminating a key reactant in sulfate attack mechanisms. The decline in performance at higher LS content (L20/M30) aligns with observations by Torres et al. (2015), who found that excessive LS can increase permeability and dilute the cementitious matrix when combined with high pozzolan contents, potentially explaining the poorer performance of the 20% LS specimen despite its high MK content.



#### 4.4 Sorptivity – 28 Days

The 28-day sorptivity performance of mortar mixes incorporating limestone powder is analyzed, as illustrated in Figure 15. shows a clear pattern of decreasing water absorption as LS content increases. The control sample (L0/M0) shows the highest absorption, followed by 10% LS replacement (L10/M0), then 15% replacement (L15/M0), with 20% LS replacement (L20/M0) showing significantly lower absorption rates throughout the test duration. For the initial absorption period (up to about  $42\text{ S}^{0.5}$ ), all samples except L20/M0 show similar steep slopes, indicating comparable initial sorptivity rates. This initial absorption primarily represents the filling of larger pores near the exposed surface. The L20/M0 sample demonstrates markedly lower initial absorption, suggesting a significant reduction in capillary pore connectivity with 20% LS replacement.

In the secondary absorption phase (from approximately  $60\text{ S}^{0.5}$  onward), all samples show a reduced slope compared to the initial phase, as expected per ASTM C1585, which distinguishes between initial and secondary absorption. During this phase, the differences between L0/M0, L10/M0, and L15/M0 become more pronounced, with clear separation in their absorption values. The 20% LS replacement sample (L20/M0) exhibits approximately half the absorption of the control mix throughout the test. This substantial reduction suggests that at this replacement level, LS significantly alters the capillary pore network structure of the mortar, likely through a combination of physical effects (filler effect) and possible chemical interactions affecting hydration products.

These results align with the ASTM C1585 standard's explanation that water absorption depends on factors including mixture proportions, cementitious component characteristics, and degree of hydration. LS appears to be effectively reducing the penetrability of the mortar's pore system, which according to the standard, would contribute to improved performance in aggressive environments where durability is concerned.

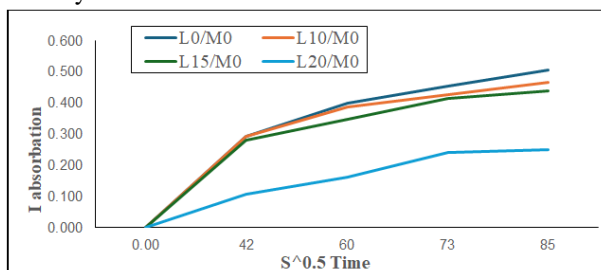


Figure 15. Effect of LS content on sorptivity at 28 days.

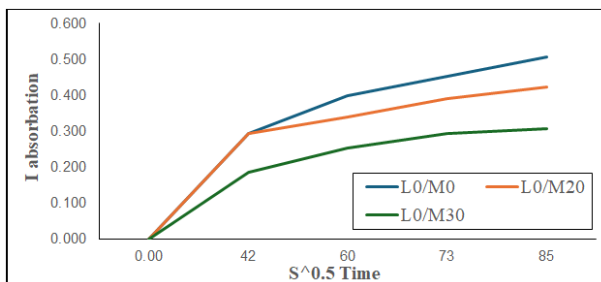


Figure 16. Effect of MK content on sorptivity at 28 days.

Figure 16 presents the results of MK mixes in 28 days. There is a clear and consistent reduction in water absorption as the MK content increases. The control sample (L0/M0) exhibits the highest absorption values throughout the test period, followed by the 20% MK replacement sample (L0/M20), with the 30% MK replacement sample (L0/M30) showing the lowest absorption. By the end of the test (at  $85\text{ S}^{0.5}$ ), the L0/M30 specimen absorbed approximately 40% less water than the control mix. The absorption patterns for all samples show two distinct phases as expected in the ASTM C1585 test: an initial steep absorption phase (up to approximately  $42\text{ S}^{0.5}$ ) followed by a more gradual secondary absorption phase. This aligns with the test method's distinction between initial and secondary absorption rates described in the standard. The initial absorption represents the rapid filling of larger near-surface pores, while the secondary absorption reflects the slower movement of water into finer capillary networks.

The significant reduction in water absorption with increasing MK content can be attributed to the pozzolanic reaction of MK with calcium hydroxide produced during cement hydration. This reaction generates additional calcium silicate hydrate (C-S-H) gel, which fills capillary pores and refines the pore structure. As described in section 4.2 of the ASTM C1585 standard, water absorption depends on factors including "mixture proportions" and "the presence of supplementary cementitious materials," which is precisely what we're observing with the metakaolin replacement. The 30% metakaolin replacement appears to provide optimal pore refinement for reducing water penetration, creating a significantly denser microstructure compared to both the control and 20% replacement samples. This suggests that at 28 days, a 30% MK replacement effectively modifies the capillary pore network to substantially reduce the penetrability of the mortar system, which would contribute to improved durability in aggressive environments as noted in section 4.1 of the standard.

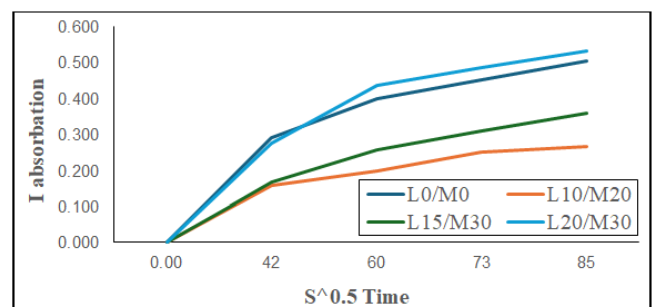


Figure 17. Effect of both LS and MK content on sorptivity at 28 days.

Figure 17 illustrates the performance of combined LS and MK mixes after 28 days in terms of water absorption. Interestingly, the L20/M30 sample shows behavior that deviates from a simple LS or MK dosage relationship. Despite having the highest total replacement level (50%), it performs worse than mixtures with lower total replacement rates. This suggests a more complex interaction between LS and MK when used together in certain proportions. At the  $42\text{ S}^{0.5}$  mark, we observe that L20/M30 and L0/M0 (control)

have nearly identical absorption values, but their behavior diverges during the secondary absorption phase. The superior performance of the L10/M20 mixture likely results from an optimal balance between the filler effect of fine LS particles and the pozzolanic reaction of metakaolin. MK reacts with calcium hydroxide produced during cement hydration to form additional C-S-H gel, while limestone particles can physically fill the spaces between cement grains and provide nucleation sites for hydration products. At the 10%/20% combination, these mechanisms appear to work synergistically to produce a denser, less permeable microstructure with reduced capillary porosity.

The L15/M30 sample shows intermediate performance, consistently better than the control and L20/M30 samples but not as effective as L10/M20. This reinforces the observation that the relationship between material proportions and performance is not simply linear, and optimal mixtures may exist at specific LS/MK ratios. These findings align with section 4.2 of the ASTM C1585 standard, which notes that water absorption depends on factors including mixture proportions and supplementary cementitious materials. The significant variability in performance among the different mixtures demonstrates the importance of carefully optimizing blend proportions when using combinations of supplementary materials to enhance durability performance.

#### 4.5 Sorptivity – 180 Days

The significant reduction in water absorption with increasing limestone content at 180 days is particularly noteworthy. At this mature age, limestone particles have likely contributed to microstructure refinement through several mechanisms. First, limestone particles act as nucleation sites that accelerate cement hydration, leading to a denser paste structure. Second, the fine limestone particles physically fill spaces between cement grains (filler effect), reducing the connectivity of the capillary pore network. Third, some calcium carbonate from the limestone may have reacted with aluminate phases in the cement to form carboaluminate phases, which can further densify the microstructure.

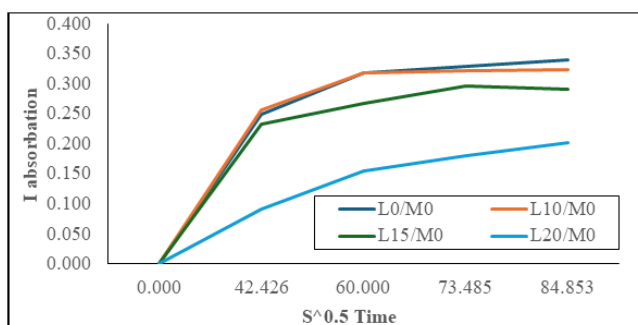


Figure 18. Effect of LS content on sorptivity at 180 days.

Figure 18 shows the effect of limestone powder content on water sorptivity after 180 days, the L15/M0 and L10/M0 samples show intermediate performance, with water absorption values between those of the control and L20/M0 samples. The consistent progression from L0/M0 to L10/M0

to L15/M0 to L20/M0 indicates a systematic improvement in water penetration resistance with increasing limestone content. This suggests that the beneficial effects of limestone on pore structure refinement scale with the replacement level, at least within the range tested. At 180 days, these effects are more pronounced than they would be at earlier ages, as the long-term physical and potential chemical contributions of limestone to microstructure development have had time to fully manifest. The continued hydration and pore refinement over time have likely enhanced the differences between the various mixtures, making the beneficial impact of limestone incorporation more evident.

These findings align with section 4.2 of the ASTM C1585 standard, which notes that water absorption depends on mixture proportions and the composition of the cementitious component. The results demonstrate that limestone incorporation can be an effective strategy for reducing the penetrability of the pore system in mature cementitious materials, potentially leading to improved durability performance in aggressive

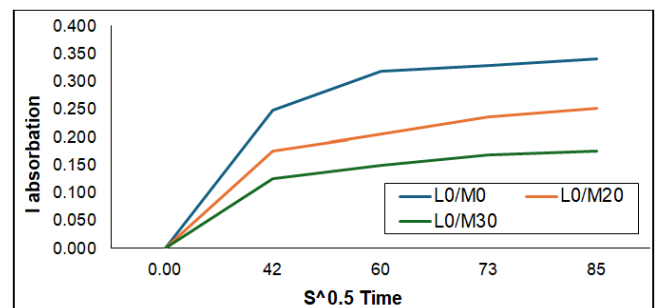


Figure 19. Effect of MK content on sorptivity at 180 days.

Figure 19 illustrates the influence of metakaolin content on water sorptivity at 180 days. We can observe a clear pattern of decreased water absorption with increasing MK content. The control sample (L0/M0) exhibits significantly higher absorption throughout the test duration compared to the MK-containing samples. The 30% metakaolin replacement (L0/M30) demonstrates the lowest absorption values, approximately half that of the control, while the 20% replacement (L0/M20) shows intermediate performance. The substantial reduction in water absorption with MK incorporation at 180 days demonstrates the long-term positive effects of this supplementary cementitious material on microstructure development. MK, being a highly reactive pozzolan, consumes calcium hydroxide produced during cement hydration to form additional calcium silicate hydrate (C-S-H) and aluminate phases. This reaction densifies the microstructure, refines the pore network, and reduces interconnectivity between capillary pores.

At 180 days, these pozzolanic reactions have progressed extensively, resulting in a mature microstructure with significantly reduced penetrability. The proportional improvement with increasing MK content (from 0% to 20% to 30%) suggests that higher replacement levels lead to more extensive pore refinement and densification. This progression aligns with the understanding that pozzolanic reactions continue long after the initial cement hydration phase, contributing to ongoing microstructural development.

The results align with section 4.2 of the ASTM C1585 standard, which notes that water absorption depends on multiple factors including mixture proportions and supplementary cementitious materials.

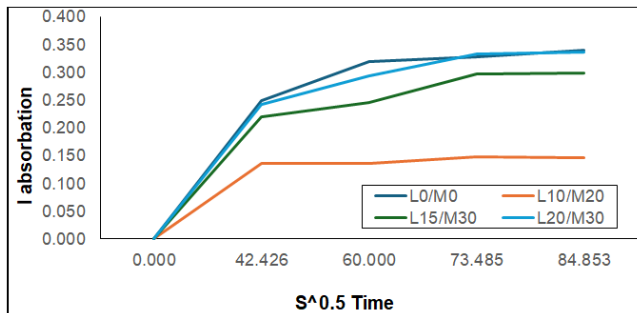


Figure 20. Effect of both LS and MK content on sorptivity at 180 days.

Figure 20, demonstrates the combined impact of LS and MK on water sorptivity after 180 days. The water absorption behavior of the various mixtures reveals a distinct hierarchical pattern. The control sample (L0/M0), with no cement replacement, exhibits the highest water absorption throughout the test. In contrast, the L10/M20 mixture (10% LS and 20% MK) shows a significant reduction in absorption, approximately 58% lower than the control. The L15/M30 and L20/M30 mixtures demonstrate intermediate performance, with reductions in absorption of 13% and 2%, respectively, compared to the control. The absorption patterns follow the typical two-phase behavior outlined in ASTM C1585, with an initial rapid absorption phase followed by a slower secondary phase. The initial phase involves the filling of larger pores near the surface, while the secondary phase reflects slower water penetration into finer capillary networks within the specimen.

A key observation is the synergistic effect between limestone and MK, which results in superior performance for the L10/M20 mixture, outperforming all other combinations, including those with higher total replacement levels. This suggests an optimal LS-to-MK ratio that maximizes pore refinement and reduces capillary connectivity.

The synergistic effect can be attributed to several mechanisms. MK, a highly pozzolanic material, reacts with calcium hydroxide from cement hydration to form additional calcium silicate hydrate (C-S-H) and aluminate phases, enhancing microstructure density and disrupting capillary pore connectivity. LS particles, on the other hand, act as nucleation sites for hydration products and can physically fill spaces between cement grains. Additionally, limestone may react with aluminate phases to form carboaluminate hydrates, further densifying the microstructure. The L15/M30 and L20/M30 mixtures, despite having higher total replacement levels, exhibit less reduction in water absorption compared to the L10/M20 mixture. This suggests that beyond certain replacement thresholds, the combined benefits of LS and MK may diminish. This could be due to a limited availability of calcium hydroxide for complete pozzolanic reactions or the dilution of the cementitious matrix, which reduces the effectiveness of the additives.

## 5. Conclusions

The experimental investigation presented in this paper allows for the illustration of the following conclusions:

- Limestone Replacement Effect:** Higher proportions of limestone powder (LS) led to decreased compressive strength, with optimal performance observed at 15% LS without additives. Limestone particles accelerate early cement hydration through their filler effect.
- Metakaolin Enhancement:** Substituting 30% of cement with metakaolin (MK) significantly enhanced compressive strength, showing approximately 30% improvement compared to control samples due to metakaolin's pozzolanic activity forming additional C-S-H.
- Optimal Combined Replacement:** The 15% LS and 30% MK combination proved most effective, achieving high compressive strength with a total replacement ratio of up to 45% of cement volume, demonstrating significant synergistic effects.
- Sulfate Resistance:** Metakaolin-containing mortars demonstrated exceptional sulfate resistance, with 30% MK replacement showing the best performance. While control samples deteriorated steadily, MK samples maintained or increased strength in sulfate environments.
- Limestone in Sulfate Exposure:** The 15% limestone replacement exhibited superior performance in sulfate environments, maintaining the lowest weight loss (1.10%) compared to other specimens, suggesting an optimal threshold exists beyond which additional limestone compromises sulfate resistance.
- Synergistic Sulfate Protection:** The L10/M20 combination (10% limestone, 20% metakaolin) showed remarkable stability in sulfate environments, maintaining approximately 35 MPa throughout the exposure period, outperforming mixtures with higher total replacement levels.
- Water Absorption Reduction:** Increasing limestone content systematically decreased water absorption, with 20% limestone replacement showing significantly lower sorptivity rates, suggesting limestone effectively alters the capillary pore network structure.
- Metakaolin Sorptivity Effect:** 30% metakaolin replacement demonstrated approximately 50% reduction in water absorption compared to control samples, indicating significant pore refinement and microstructure densification.
- Optimal Blend for Sorptivity:** The L10/M20 mixture showed superior performance in reducing water absorption, outperforming combinations with higher total replacement levels, indicating an optimal limestone-to-metakaolin ratio exists for maximizing pore refinement.
- Maturation Effects:** At 180 days, the benefits of cement replacements were more pronounced than at earlier ages, as the physical and chemical contributions of limestone and metakaolin to microstructure development fully manifested over time.

## REFERENCES

- [1] Darko, A.; Chan, A.P.; Owusu-Manu, D.-G.; Ameyaw, E.E. Drivers for implementing green building technologies: An international survey of experts. *J. Clean. Prod.* 2017, 145, 386–394. [CrossRef]
- [2] Dimitriou, G.; Savva, P.; Petrou, M.F. Enhancing mechanical and durability properties of recycled aggregate concrete. *Constr. Build. Mater.* 2018, 158, 228–235. [CrossRef]
- [3] S.W. Tang, Y. Yao, C. Andrade, Z.J. Li, Recent durability studies on concrete structure, *Cem. Concr. Res.* (2015)
- [4] Parvathy, C. Karthika, V. Gayathr, Experimental studies on durability aspects of high strength concrete using flyash and alccofine, *Int. J. Recent Technol. Eng.* 7 (2018) 423–427.
- [5] European Federation of National Associations Aggregates for mortar EN 13139(2018) Aggregates for mortar
- [6] G. Moir, S. Kelham, Developments in manufacture and use of Portland limestone cement, in: V.M. Malhotra (Ed.), *Proceedings of High-Performance Concrete*, ACI SP-172, American Concrete Institute, Detroit, MI, 1997, pp. 797–819.
- [7] H.M. Bustnes, B. Lagerblad, E. Forssberg, The function of fillers in concrete, *Mater. Struct.* 37 (2004) 74–81.
- [8] I.Soroka, N. Setter, The effect of fillers on strength of cement mortars, *Cem. Concr. Res.* 7 (1977) 449–456.
- [9] I.Soroka, N. Stern, Calcareous fillers and the compressive strength of Portland cement, *Cem. Concr. Res.* 7 (4) (1976) 449–456.
- [10] H. Moosberg, B. Lagerblad, E. Forssberg, The function of fillers in concrete, *Mater. Struct.* 37 (2004) 74–81.
- [11] J.J. Thomas, H.M. Jennings, J.J. Chen, Influence of nucleation seeding on the hydration mechanisms of tricalcium silicate and cement, *J. Phys. Chem.* 113 (11) (2009) 4327–4334.
- [12] M. Hubler, H. Jennings, J. Thomas, Influence of nucleation seeding on the compressive strength of ordinary portland cement and alkali activated blast furnace slag, *Infrastructure Technology Institute Year 2 Final Report*, Northwestern University, 1976. Hafez
- [13] Hewlett, P.C. and Peter, C. (1997) *Chemistry of Cement and Concrete*, Hewlett, P.C. (Ed.): Butterworth – Heinemann, 1053 pages.
- [14] Rifai, R.I., El-Miligy, A., Seleim, A.H. and Abo El-Safa, M. (2002a) 'Geotechnical evaluation of the red clay deposits of Abu Darag-Qiseib area, for cement industry, Gulf of Suez, Egypt', *Annals Geol. Surv. Egypt*, Vol. XXV, pp.549–558.
- [15] G.C. Isaia, A.L.G. Gastaldini and R. Moraesl, "Physical and pozzolanic action of mineral additions on the mechanical strength of high-performance concrete", *Cement and Concrete Composites*, Vol. 25, Issue 1, PP. 69-76, January 2003, [https://doi.org/10.1016/S0958-9465\(01\)00057-9](https://doi.org/10.1016/S0958-9465(01)00057-9)
- [16] M Tirumala Rao and Dumpa Venkateswarlu "Experimental Investigate of Strength Parameters of Concrete under Acidic Environment" *International Journal of Engineering and Advanced Technology (IJEAT)* ISSN: 2249-8958 (Online), Vol.8, Issue-6, PP. 3865-3869, 30August 2019.
- [17] Bentz, D.P., Irassar, E.F., Bucher, B.E., & Weiss, W.J. (2017). Limestone and silica powder replacements for cement: Early-age performance. *Cement and Concrete Composites*, 78, 43-56.
- [18] Bonavetti, V., Donza, H., Menéndez, G., Cabrera, O., & Irassar, E.F. (2003). Limestone filler cement in low w/c concrete: A rational use of energy. *Cement and Concrete Research*, 33(6), 865-871.
- [19] De Weerd, K., Kjellsen, K.O., Sellevold, E., & Justnes, H. (2011). Synergy between fly ash and limestone powder in ternary cements. *Cement and Concrete Composites*, 33(1), 30-38.
- [20] Khatib, J.M., & Wild, S. (1998). Sulphate resistance of metakaolin mortar. *Cement and Concrete Research*, 28(1), 83-92.
- [21] Poon, C.S., Kou, S.C., & Lam, L. (2006). Compressive strength, chloride diffusivity and pore structure of high performance metakaolin and silica fume concrete. *Construction and Building Materials*, 20(10), 858-865.
- [22] Sabir, B.B., Wild, S., & Bai, J. (2001). Metakaolin and calcined clays as pozzolans for concrete: a review. *Cement and Concrete Composites*, 23(6), 441-454.
- [23] Wild, S., Khatib, J.M., & Jones, A. (1996). Relative strength, pozzolanic activity and cement hydration in superplasticised metakaolin concrete. *Cement and Concrete Research*, 26(10), 1537-1544.
- [24] Antoni, M., Rossen, J., Martirena, F., & Scrivener, K. (2012). Cement substitution by a combination of metakaolin and limestone. *Cement and Concrete Research*, 42(12), 1579-1589.
- [25] Lothenbach, B., Le Saout, G., Gallucci, E., & Scrivener, K. (2008). Influence of limestone on the hydration of Portland cements. *Cement and Concrete Research*, 38(6), 848-860.
- [26] Vance, K., Aguayo, M., Oey, T., Sant, G., & Neithalath, N. (2013). Hydration and strength development in ternary portland cement blends containing limestone and fly ash or metakaolin. *Cement and Concrete Composites*, 39, 93-103.
- [27] Skaropoulou, A., Tsivilis, S., Kakali, G., Sharp, J. H., & Swamy, R. N. (2013). Long term behavior of Portland limestone cement mortars exposed to magnesium sulfate attack. *Cement and Concrete Composites*, 31(2), 158-165.
- [28] Irassar, E. F. (2009). Sulfate attack on cementitious materials containing limestone filler - A review. *Cement and Concrete Research*, 39(3), 241-254.
- [29] Courard, L., Darimont, A., Schouterden, M., Ferauche, F., Willem, X., & Degeimbre, R. (2003). Durability of mortars modified with metakaolin. *Cement and Concrete Research*, 33(9), 1473-1479.
- [30] Santhanam, M., Cohen, M.D., & Olek, J. (2003). Effects of gypsum formation on the performance of cement mortars during external sulfate attack. *Cement and Concrete Research*, 33(3), 325-332.
- [31] Siddique, R., & Klaus, J. (2009). Influence of metakaolin on the properties of mortar and concrete: A review. *Applied Clay Science*, 43(3-4), 392-400.
- [32] Vejmelková, E., Pavlíková, M., Keppert, M., Keršner, Z., Rovnaníková, P., Ondráček, M., Sedlmajer, M., & Černý, R. (2012). High performance concrete with Czech metakaolin: Experimental analysis of strength, toughness and durability characteristics. *Construction and Building Materials*, 26(1), 1014-1024.
- [33] Irassar, E.F., Bonavetti, V.L., & González, M. (2010). Microstructural study of sulfate attack on ordinary and limestone Portland cements at ambient temperature. *Cement and Concrete Research*, 40(3), 470-478.
- [34] Lothenbach, B., Scrivener, K., & Hooton, R.D. (2011). Supplementary cementitious materials. *Cement and Concrete Research*, 41(12), 1244-1256.
- [35] Schmidt, T., Lothenbach, B., Romer, M., Scrivener, K., Rentsch, D., & Figi, R. (2009). A thermodynamic and experimental study of the conditions of thaumasite formation. *Cement and Concrete Research*, 39(2), 115-125.
- [36] Skaropoulou, A., Sotiriadis, K., Kakali, G., & Tsivilis, S. (2013). Use of mineral admixtures to improve the resistance of limestone cement concrete against thaumasite form of sulfate attack. *Cement and Concrete Composites*, 37, 267-275.
- [37] Al-Akhras, N.M. (2006). Durability of metakaolin concrete to sulfate attack. *Cement and Concrete Research*, 36(9), 1727-1734.
- [38] Siddique, R., & Klaus, J. (2009). Influence of metakaolin on the properties of mortar and concrete: A review. *Applied Clay Science*, 43(3-4), 392-400.
- [39] Fernandez, R., Martirena, F., & Scrivener, K.L. (2012). The origin of the pozzolanic activity of calcined clay minerals: A comparison between kaolinite, illite and montmorillonite. *Cement and Concrete Research*, 41(1), 113-122.
- [40] Kadri, E.H., Kenai, S., Aggoun, S., Siddique, R., & Kadri, A. (2011). Influence of metakaolin and silica fume on the heat of hydration and compressive strength development of mortar. *Applied Clay Science*, 53(4), 704-708.
- [41] Torres, S.M., Sharp, J.H., Swamy, R.N., Lynsdale, C.J., & Huntley, S.A. (2015). Long term durability of Portland-limestone cement mortars exposed to magnesium sulfate attack. *Cement and Concrete Composites*, 52, 64-74.
- [42] Shamaa, A., El-Dakoury, A., & Helmy, I. (2016). Durability performance of cement composites containing limestone and metakaolin under sulfate attack. *Cement and Concrete Composites*, 67, 25–34.