e-ISSN: 2564-7954 CUSJE 21(01): 042-053 (2024) Research Article

Çankaya University

Journal of Science and Engineering

https://dergipark.org.tr/cankujse

CUJSE

Comparative Study of Metakaolin-Quicklime and Metakaolin-Bacillus Subtilis as Self-Healing Agents in Concrete

Grace Modupeola Amusan[1], and Ganiu Aremu Adeagbo[1*]

[1] Department of Civil Engineering, Olabisi Onabanjo University, Ago-Iwoye, Nigeria

Keywords

Self-Healing Agents, Compressive Strength, Flexural Strength, Crack Healing.

Abstract

The study examined the physical, mechanical, and crack-healing properties of concrete produced using Metakaolin-Bacillus subtilis and Metakaolin-Quicklime as self-healing agents. Two concrete specimens of grade M30 were produced; the first specimens were prepared incorporating metakaolin and quicklime of replacement percentages of 5, 10, and 15 by weight of cement, respectively, and the second, incorporating metakaolin of the same replacement percentages and 10 ml *Bacillus subtilis.* The mechanical properties were conducted at 28 days on concrete cubes of size 150 × 150 × 150 (mm^3) and concrete beams of size 400 × 100 × 100 (mm^3). The self-healing efficiency was evaluated through crack induction, and subsequent analyses included a comparative examination of the crack closure mechanisms for each agent. The compressive strength at 28 days' curing age showed that 10% replacement of metakaolin-bacillus subtilis yields the best strength of 41.2 MPa, a 17.8% increase over the control specimen. Also, the combined blend of metakaolin and quicklime showed the highest strength at 10% replacement, which gained a 53% increase over the control specimen. The comparative analysis between metakaolin-quicklime and metakaolin-Bacillus subtilis reveals that both combinations exhibit self-healing properties through different mechanisms. In conclusion, the study establishes the efficacy of metakaolin, quicklime, and Bacillus subtilis as promising self-healing agents in concrete, showcasing their unique mechanisms and paving the way for enhanced durability and structural integrity in construction applications.

1. Introduction

Concrete, as the foundation of modern construction, is renowned for its incredible strength and ability to withstand the test of time, making it the go-to choose for builders and engineers in the construction industry. However, despite its durability, concrete structures can develop cracks over time due to various factors, including shrinkage, temperature fluctuations, and external loads. These cracks can compromise the integrity of the concrete, leading to reduced service life and increased maintenance costs [1-6]. To address this challenge, researchers have been exploring innovative approaches to enhance the self-healing capacity of concrete, drawing inspiration from the healing abilities of living organisms [2, 5].

Jo *et al.* [7] have explored the effect of metakaolin on the durability properties of self-healing concrete, they observed enhanced resistance to chloride ion penetration, reduced water permeability, and improved resistance to sulfate attack [7]. Similarly, Li *et al.* [8] studied the impact of metakaolin on the crystalline healing of concrete, they observed that metakaolin accelerated the growth of calcium carbonate crystals, leading to improved crack closure and water tightness [8]. Han *et al.* [9] conducted an experimental study to evaluate the impact of metakaolin on the autogeneous healing of concrete. These results indicated that metakaolin significantly

* Corresponding Author: adeagboganiu2001@gmail.com
Received: March 06, 2024, Accepted: April 21, 2024

enhanced the self-healing capacity of concrete, promoting crack closure and improving the overall mechanical performance [9].

According to Jonkers *et al.* [4], the vulnerability of concrete to cracking is influenced by various factors, including inadequate tensile strength, low resistance, insufficient ductility, and high compression properties [4]. The authors found that the inclusion of particular organic mineral precursor chemicals and spore-forming alkaliphilic bacteria as self-healing agents produces calcite particles up to 100 m in size, which have the capacity to seal small to even bigger cracks [4]. In a study, conducted by Kalhori and Bagherpour [10], the impact of bacillus subtilis on the healing process and the mechanical characteristics of concrete was assessed. Bacteria was added to the mix design and curing solution to study the effect on strength, durability, and healing of concrete specimens [10].

The findings of an experimental investigation conducted to assess the impact of two types of bacteria, sporosarcina pasteurii and bacillus subtilis, with different cell concentration on the water absorption of four types of concrete aggregates revealed that the surface deposition of calcium carbonate crystals reduced water absorption by 20 to 30 percent [11]. In the work of Farhadi et al. [12], impacts of bacterial on compressive strength of concrete, different bacterial were studied but for the purpose of this research focuses will be on bacillus subtilis that was also used, the concentration used in their study was 2.8×10^8 cells/cm^3 and the result shows there was 12% increase in the compressive strength of the concrete compared to the controlled concrete sample used.

Recent studies have centered on exploring the mixed effect of metakaolin and Bacillus subtilis in self-restoration concrete to optimize healing performance and concrete overall performance. The results proven that the presence of each substance brought about advanced crack restoration and tremendous improvements on mechanical strengths, indicating a superb synergy between metakaolin and Bacillus subtilis [13,14]. Additionally, Gharzouni *et al.*, [15] conducted a study on the outcomes of metakaolin and Bacillus subtilis on the mechanical residences of concrete and the organic healing process. The use of metakaolin was found to favour the conditions for bacterial activity, resulting in greater large crack recuperation and progressed mechanical overall performance of the concrete [15].

Similarly, Lee *et al.* [16] investigated the simultaneous use of metakaolin and Bacillus subtilis in self-restoration concrete and observed stepped forward of mechanical properties and impact resistance of the concrete with each additive. Dall'Igna *et al.* [17] centered on the impact of metakaolin and Bacillus subtilis on decreasing crack widths in self-recovery concrete, finding that the aggregate of those components effectively minimized crack widths and not on time crack propagation [17]. Furthermore, metakaolin and Bacillus subtilis addition had been utilized to resist freeze-thaw cycles and de-icing salts in concrete under competitive exposure conditions. Coppola et al. [18] submitted that metakaolin and Bacillus subtilis addition in concrete had a more desirable resistance to freeze-thaw cycles and de-icing salts, making sure of its prolonged service lifespan [18].

Although, studies on the combination of Metakaolin and Bacillus subtilis in self-recuperation concrete keep on revealing promising outcomes and paving the way for more resilient and robust concrete structures, further research and practical applications are needed for brighter future infrastructure development. Therefore, this study explores the novel application of Metakaolin-Bacillus subtilis (MBs) and Metakaolin-Quicklime (MQ) as self-healing agents in concrete. The research aims to advance self-healing concrete technology for better strength and durability of concrete structures. The study seeks to develop sustainable and self-healing concrete suitable for practical applications in civil engineering construction.

Self-healing concrete is promising concrete. Traditionally, repairing and remediation techniques for concrete are expensive and time-consuming; self-healing concrete, an attractive alternative, is a bacterial concrete, which employs a bio-mineralization mechanism to address cracks [6]. Self-healing concrete structures has the potential to extend the service life of structures, reduce maintenance costs, enhance the sustainability of the built environment, and revolutionize the design and construction of critical infrastructure systems [4]. Thus, this research aims to examine Metakaolin-Bacillus subtilis and Metakaolin-Quicklime as materials with self-healing capabilities for concrete sustainability solutions.

2. Experimental Study

2.1. Materials

For the experimental study, Ordinary Portland Cement (OPC), metakaolin and quicklime were used as binding material. Fine and coarse aggregates were selected according to local standards. Metakaolin and quicklime were chosen as the supplementary cementitious material (SCM). The metakaolin was produced by calcining kaolin clay for 700 ^{o}C for 3 hrs, sieved using 0.063 microns sieve. Superplasticizer was used as addictive. Bacillus subtilis bacteria cultured from locust beans production effluent was also used as a biological healing agent.

The cement was of grade 42.5 N with a specific gravity of 3.15, and the metakaolin with a specific gravity of 2.13 was used. The fine aggregate was well-graded river sand that was dry, clean, and free of unsuitable particles. Its specific gravity is 2.47. Granite was used as the coarse material; with aggregate size maximum of 12.5 mm. The coarse aggregate was angular and dry. The clean water used to mix the concrete was devoid of organic compounds, oils, acids, and alkalis. Plate 1 depicted Bacillus subtilis grown from locus bean wastewater on the slant.

Plate 1. Image of *bacillus subtilis* algae on the slant.

2.2. Production of Metakaolin-Quicklime and Metakaolin-Bacillus Subtilis Self-Healing Concretes

2.2.1. Production of Metakaolin-Quicklime Concrete

Concrete specimens of grade M30 with cement contents (394 kg/m^3) and water content (157.6 kg/m^3) were batched, and metakaolin and quicklime were added at different replacement percentages of 0, 5, 10, and 15 by weight of the cement as presented in Table 1. In compliance with the applicable standard requirements, tests were performed on the materials, including the specific gravity test, the workability test on the freshly produced concrete, and the particle size distribution on the aggregates [19, 21, 22]. The mixes were cast into concrete cubes and beams with dimensions of 150 × 150 × 150 (mm^3) and 400 × 100 × 100 (mm^3), respectively. They were cured by immersing them in water for seven and twenty-eight days. The specimen was put through mechanical testing as well as tests for the effectiveness of crack healing.

2.2.2. Production of Metakaolin-Bacillus Subtilis Concrete

Concrete specimens of grade M30 with cement content (394 kg/m^3) and water content (157.6 kg/m^3) were batched. Metakaolin was added at different replacement percentages of 0, 5, 10, and 15% by weight of the cement, as presented in Table 2; a constant dosage of 10 ml of Bacillus subtilis was used for the mix. Tests were carried out on the materials, such as the specific gravity test, particle size distribution on the aggregates, and workability test on the fresh concrete in accordance with relevant standard codes [19 - 21]. The mixes were cast into concrete cubes and beams with dimensions of 150 × 150 × 150 (mm^3) and 400 × 100 × 100 (mm^3), respectively. They were cured by immersing them in water for seven and twenty-eight days. The specimens underwent mechanical testing as well as efficiency tests for crack healing.

Table 1. Mix proportion of metakaolin-quicklime (MQ) concrete (kg/m^3)

Ingredients	***0% MQ***	***5% MQ***	***10% MQ***	***15% MQ***
Cement	394	354.6	315.2	275.8
Metakaolin	-	19.7	39.4	59.1
Quicklime	-	19.7	39.4	59.1
Fine aggregate	791	791	791	791
Coarse aggregate	1068	1068	1068	1068
Superplasticizer	2.675	2.675	2.675	2.675
Water	157.6	157.6	157.6	157.6

Table 2. Mix proportion of metakaolin-*bacillus subtilis* (MBs) concrete (kg/m^3)

Ingredients	***0% MBs***	***5% MBs***	***10% MBs***	***15% MBs***
Cement	394	374.3	354.6	334.9
Metakaolin	-	19.7	39.4	59.1
Bacillus subtilis (ml)	10	10	10	10
Fine aggregate	791	791	791	791
Coarse aggregate	1068	1068	1068	1068
Superplasticizer	2.675	2.675	2.675	2.675
Water	157.6	157.6	157.6	157.6

2.3. Test on Materials and Fresh Concrete

Chemical analysis was carried out on the Metakaolin to determine the material pozzolanicity. Particle size analysis was performed on the aggregates to ascertain the fineness and ease of characterization of the aggregates. Sieve analysis was carried out on both fine and coarse aggregates in accordance with BS882 [19]. The aggregate sample's passing percentage was computed and displayed against particle size. The standard code [19] was followed for conducting the test. Additionally, slump test was carried out to determine the degree of workability of the fresh concrete. The test was carried out in compliance with the reference code in BS1881 [21].

2.4. Test on Hardened Concrete

Compressive strength test was tested on concrete cubes measuring 150 mm × 150 mm × 150 mm at 7 and 28 days using a digital hydraulic compression testing machine with a load capability of 2000 kN. The test cube was put under the hydraulic press, and each specimen's stress at failure was noted as the load was applied until the specimen failed. The test was carried out in compliance with BS 1881 guidelines [22]. Consequently, flexural strength test was performed using a hydraulic flexural testing machine, concrete beams with dimensions of 400 mm by 100 mm by 100 mm were evaluated for flexure at seven and twenty-eight days of cure. Forty-eight specimens were tested in all. The flexural test was carried out in compliance with BS 1881 guidelines [23].

2.5. Crack Healing Efficiency Test

150 mm × 150 mm × 150 mm cubes were used in the tests to assess the crack and the material's capacity to mend it. On the cube specimens, cracks with the same length and depth were induced in the same direction. Six concrete cubes were used. At days three, seven, and twenty-eight, the cracks were seen and measured. The fracture healing test was carried out in compliance with ISO 18477 standards [24].

3. Results and Discussion

3.1. Chemical Properties of Metakaolin

The results of the chemical analysis conducted on Metakaolin revealed that, the addition of the three primary chemical constituents, silicon dioxide (SiO_2), aluminium oxide (Al_2O_3) and iron oxide (Fe_2O_3) are dominant, with concentration equivalent of 92.38% while in Quicklime CaO is most dominant with a value of 92.10%, the values are greater than 70% specified for pozzolanic materials in ASTM C618 [25].

Table 3. Chemical properties of Metakaolin (MK) and Quicklime (QL)

Constituent	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	T_iO_2	LOI
MK (%)	54.50	34.81	3.07	0.34	1.03	1.21	0.17	0.02	1.25
QL (%)	1.79	0.29	0.34	92.10	1.20	0.03	0.01	-	3.57

3.2. Particle Size Distribution

The well-graded fine and coarse aggregates in Figures 1 and 2 are demonstrated by their curves, which also have coefficients of curvature greater than one. Figures 1 and 2, respectively, show the fine and coarse aggregate particle size distributions.

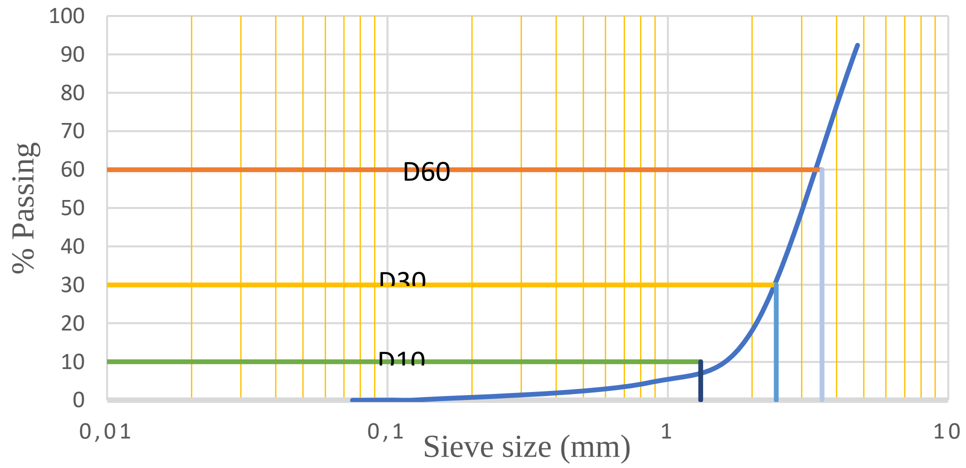

Figure 1. Particle size distribution curve of fine aggregate.

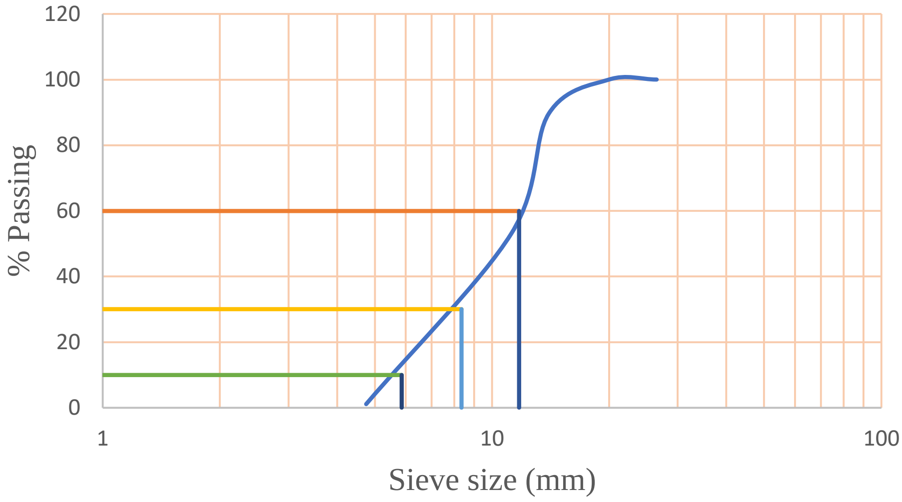

Figure 2. Particle size distribution curve of coarse aggregate.

3.3. Slump Test Results

The results of the slump in Table 4 show that the overall workability is good for all the mixes. However, as the percentage replacement of the additives increases, the slump decreases. C-F-7 represent the mix of concrete for 7 days curing while C-F-28 represent the mix of concrete for 28 days curing age.

Table 4. Slump results of the concrete

Specimen Mix	*% Metakaolin & quicklime replacement*	*Water/binder ratio*	*Superplasticizer/ binder ratio*	*Slump (mm)*
C-F-7	0%	0.4	0.08	140
C-F-7	5%	0.45	0.035	120
C-F-7	10%	0.50	0.030	120
C-F-7	15%	0.45	0.035	100
C-F-28	0%	0.4	0.08	140
C-F-28	5%	0.45	0.035	110
C-F-28	10%	0.45	0.035	90
C-F-28	15%	0.45	0.035	100

3.4. Compressive Strength Results

Figure 3 shows the result for average compressive strength of metakaolin-quicklime (Mk+QL) concrete at 7 and 28 days curing age; from the experimental findings, the combined blends of metakaolin and quicklime increased compressive strength over the control specimen, the results show that the lowest percentage of replacements gave better performance. 5% replacement specimens showed 17.8% strength gained over control specimens at 28 days curing age.

Figure 4 shows the average compressive strength of metakaolin-bacillus subtilis (Mk+Bs) concrete at 7 and 28 days curing age. From the experimental findings, increasing the replacement of metakaolin led to strength enhancement the bacterial improved strengths over metakaolin mixes. Best performance was 10% metakaolin replacement and 10 ml dosage of *Bacillus subtilis*. Figures 5 and 6 compared the metakaolin-quicklime and metakaolin-bacillus subtilis concretes at 7 and 28 days curing ages, respectively. This is in agreement with Farhadi *et al*. [12]; Kalhori and Bagherpour [10].

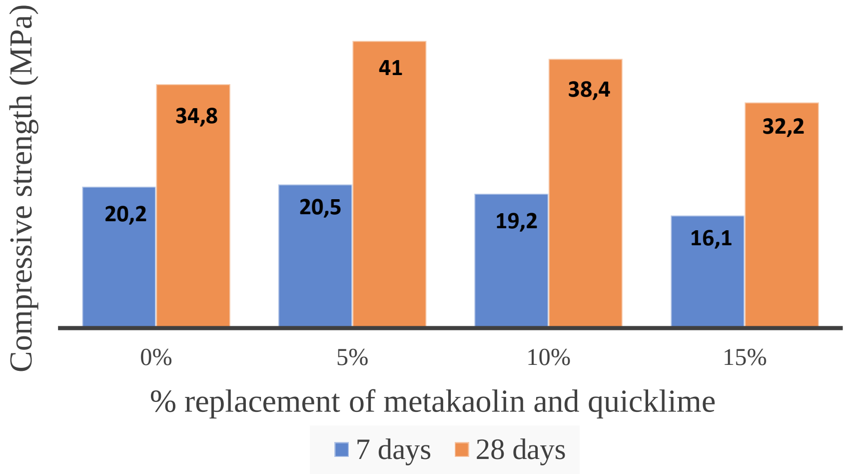

Figure 3. Compressive strength results of metakaolin-quicklime concrete.

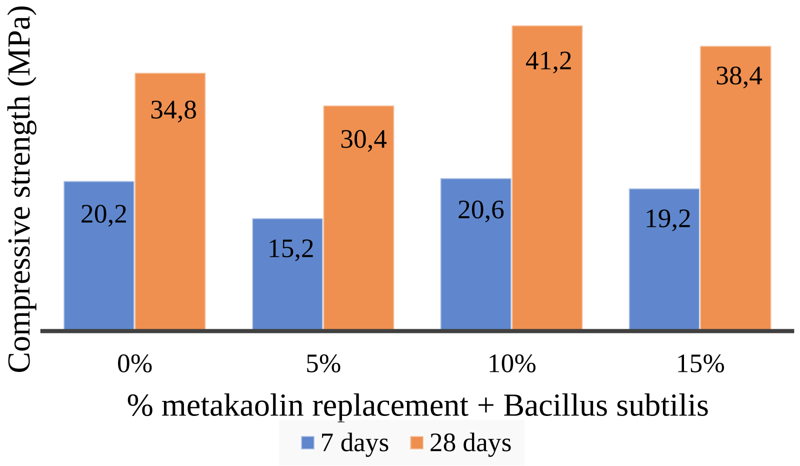

Figure 4. Compressive strength results of metakaolin-bacillus subtilis concrete.

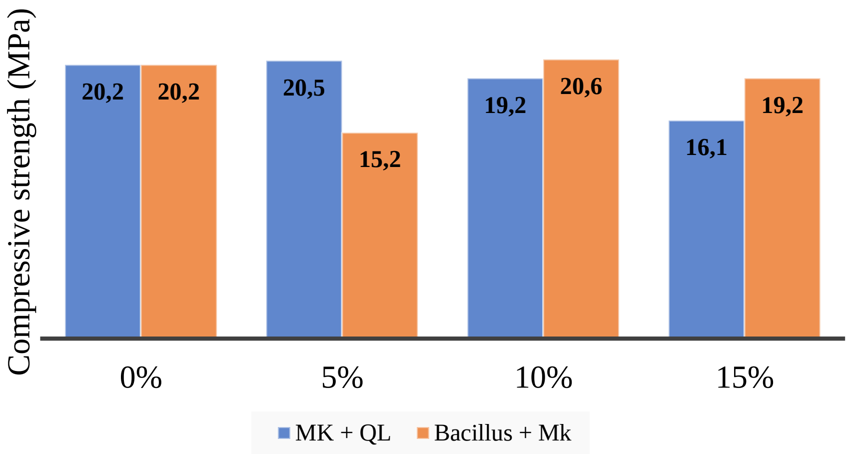

Figure 5. Compressive strength results variations at 7 days curing age.

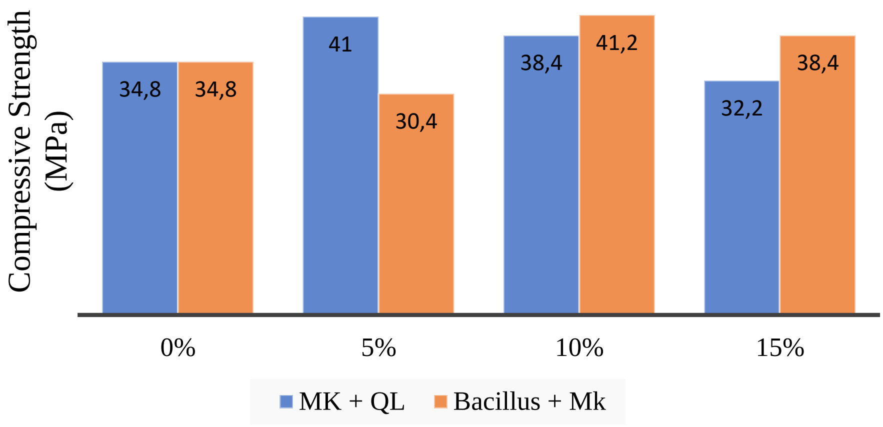

Figure 6. Compressive strength results variations at 28 days curing age.

3.5. Flexural Strength Results

Figure 7 shows the average flexural strength of metakaolin-quicklime (Mk+QL) concrete; from the experimental findings, the combined blend of metakaolin and quicklime showed improved strength over the control specimen, and the 10% combined blend showed a 53% increase in strength over the control specimen. Figure 8 shows the average flexural strength of metakaolin-bacillus subtilis (MK+Bs) concrete; from the experimental findings, increasing metakaolin replacement increased flexural strengths, and *bacillus subtilis* enhanced strength over metakaolin alone. The combination showed the best performance for 10% metakaolin content and improvement more significant at 28 days curing age. This agrees with Yamasamit *et al.* [14].

Figures 9 and 10 compare the flexural strength of metakaolin-quicklime (Mk+QL) and metakaolin-bacillus subtilis (Mk+Bs) concrete. The results show that the blend of metakaolin-quicklime and metakaolin-bacillus subtilis displayed a significant improvement in the flexural strength compared to control specimen. The blend of metakaolin-quicklime (MK+QL) has the highest flexural strength of 30.12 MPa at 10% replacement to the weight of the cement.

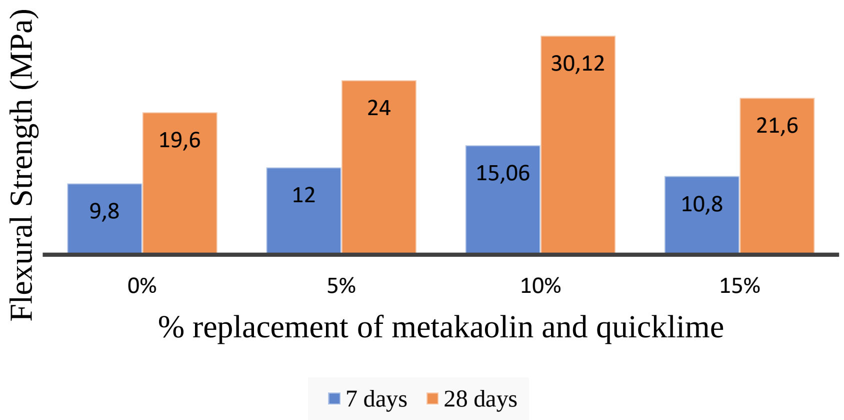

Figure 7. Average flexural strength results for metakaolin-quicklime concrete.

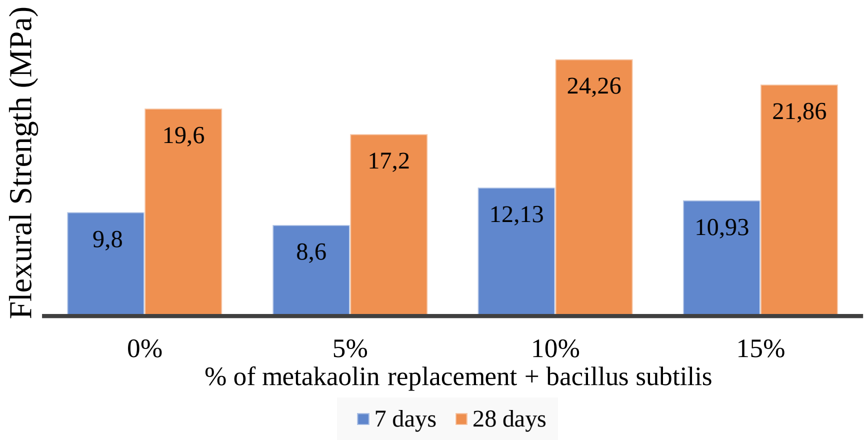

Figure 8. Average flexural strength results for metakaolin-bacillus concrete.

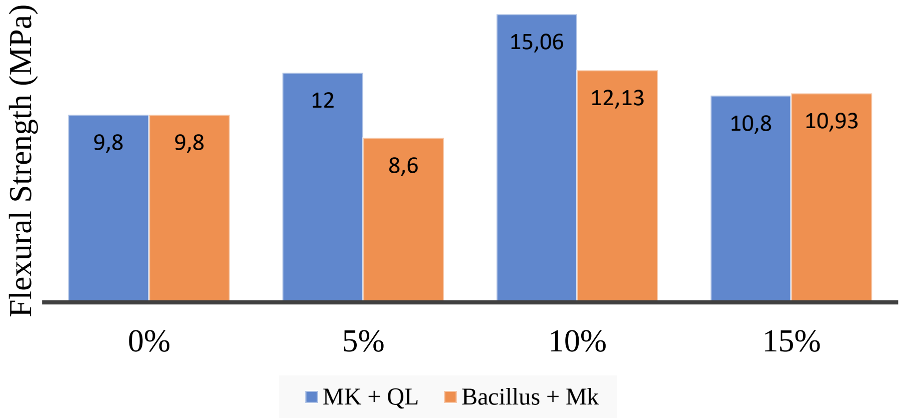

Figure 9. Comparison of flexural strength results at 7 days curing age.

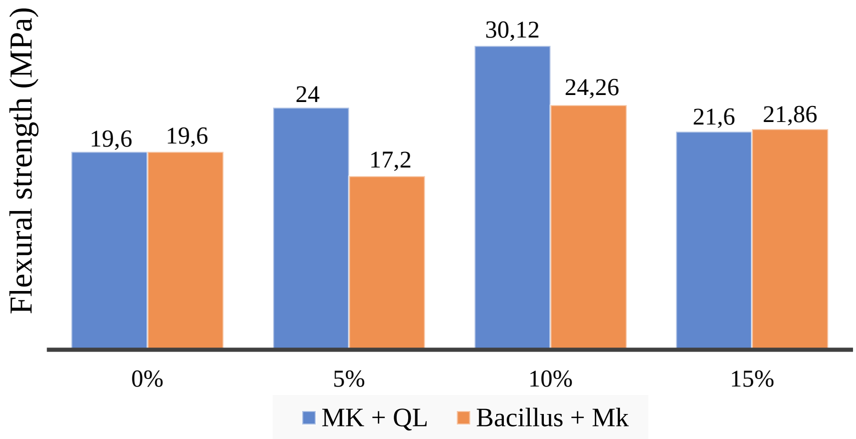

Figure 10. Comparison of flexural strength results at 28 days curing age.

3.6. Crack Healing Efficiency Results

Table 5 compares the crack healing of metakaolin-quicklime (MK+QL) and metakaolin-bacillus subtilis (MK+Bs) concrete at 0, 3, 7, 14, and 28 days curing ages to evaluate their self-healing properties. The crack monitoring revealed distinct differences in the healing process between the control samples and those with metakaolin and *Bacillus subtilis*. The control samples exhibited limited crack closure, whereas the samples with metakaolin showed more efficient crack healing. Notably, the specimens containing both metakaolin and *Bacillus subtilis* exhibited the most substantial healing. The microbial-induced calcite precipitation by *Bacillus subtilis* played a critical role in closing the cracks, particularly in conjunction with metakaolin. The comparative analysis between metakaolin-quicklime (Mk+QL) and metakaolin-Bacillus (MK+Bs) subtilis reveals that both combinations exhibit self-healing properties, albeit through different mechanisms. Understanding the conditions under which each combination excels provides valuable insights for tailoring self-healing concrete formulations based on project requirements, environmental considerations, and economic factors. This is in agreement with Li *et al.* [8].

Table 5. Comparison of healing combination of bacillus subtilis and metakaolin & combination of quicklime, bacillus subtilis, and metakaolin as self-healing agents.

Days	*% of healing for Mk & QL*	*% of healing for MK & Bacillus subtilis*
0	0	0
3	5	9.7
7	11.7	22.6
14	23.3	45.2
28	46.7	90.3

3.7. Discussions

The study findings unequivocally demonstrate the efficacy of Metakaolin-Bacillus subtilis (Mk+Bs) and Metakaolin-Quicklime (MK+QL) as self-healing agents in concrete. The inclusion of these materials has led to a significant improvement in crack-healing efficiency, with both formulations exhibiting markedly better mechanical properties than control specimens. The increased efficiency of these self-healing agents can be attributed to the unique properties of metakaolin, Bacillus subtilis, and quicklime.

Metakaolin performs as a supplementary cementitious material, supporting the formation of extra hydration products, and reducing concrete permeability. Bacillus subtilis catalyzes the precipitation of calcium carbonate in cracks, effectively sealing them and preventing further propagation. Quicklime reacts with water to produce calcium hydroxide, which fills cracks and enhances the overall integrity of the concrete matrix.

The study results highlight the potential of metakaolin-Bacillus subtilis and metakaolin-quicklime as viable self-healing agents for concrete. By leveraging the unique properties of these materials, it is possible to develop sustainable concrete solutions that exhibit enhanced durability and longevity. Therefore, future research efforts should focus on optimizing the formulation and application of these self-healing agents for concrete in severe condition of exposure, self-curing concrete, and practical implementation in construction projects, thereby revolutionizing the future of concrete technology.

4. Conclusion

The Comparative Study of Metakaolin, Quicklime, and Bacillus subtilis as Self-Healing Agents in Concrete project has provided valuable insights into the efficacy of these agents in enhancing the self-healing properties of concrete. Through a systematic investigation, metakaolin, quicklime, and Bacillus subtilis exhibit distinct mechanisms for promoting self-healing in concrete. Metakaolin contributes to forming additional C-S-H gel, quicklime promotes autogenous healing through calcium carbonate precipitation, and Bacillus subtilis induces calcite formation via microbial activity. The comparative analysis indicates variations in the efficiency of these agents in repairing cracks and improving the overall durability of concrete. The combined use of metakaolin and quicklime showed a better performance in their self-healing efficiency compared to the combined blend of metakaolin and quicklime.

The effectiveness of each self-healing agent is influenced by factors such as concentration, activation methods, and curing conditions. Optimal parameters for applying these agents must be carefully considered to maximize their healing potential. The compatibility of metakaolin, quicklime, and Bacillus subtilis with different concrete mixtures is crucial for their successful integration into construction practices. Understanding how these agents interact with various concrete compositions is essential for practical applications. While short-term self-healing capabilities have been observed, further research is needed to assess the long-term durability and stability of the repaired concrete structures. Monitoring the performance of these agents over an extended period under real-world conditions will provide valuable data for their practical implementation.

Declaration of Competing Interest

No conflict of interest was declared by the authors.

Authorship Contribution Statement

Grace Modupeola Amusan: Writing, Reviewing, Data Preparation, and Editing.

Ganiu Adeagbo: Writing, Reviewing, Data Preparation, and Editing.

References

[1] M. Azam, N. Ghabbour, S. Ahmed, and A. Hosny, “Evaluation of metakaolin’s pozzolanic activity and its impact on microstructure of self-healing concrete.” *Construction and Building Materials,* vol. 207, pp. 93-104, 2019.

[2] S. V. Kulkarni, and P. G Koppad, “Self-Healing Concrete: A Comprehensive Review.” *Construction and Building Materials,* vol. 176, pp. 478-495, 2018.

[3] X. Luo, N. Han, T. Ngo, and P. A. Mendis, “Review on the Use of Metakaolin in Cement-Based Materials.” *Construction and Building Materials,* vol. 124, pp. 676-690, 2016.

[4] H. M. Jonkers, “Bacteria-based self-healing concrete.” *Heron.*, vol. 56, no. ½, pp. 1-12, 2011.

[5] K. V. Tittelboom, and D. B. Nele, “Self-healing in cementitious materials-a review.” *Materials*, vol. 6, no. 6, pp. 2182-2217, 2013.

[6] M. Santhanam, M. D. Cohen, and J. Olek, “Microstructure, and properties of metakaolin concrete: A state-of-the-art review.” *Cement and Concrete Composites,* vol. 33, no. 2, pp. 110-121, 2011.

[7] B. W. Jo, and G. H. Kim, “A review on the role of metakaolin in concrete.” *Construction and Building Materials,* vol. 209, pp. 233-242, 2019.

[8] Z. Li, J. Zhou, Y. Wang, and T. Ji, “Metakaolin-induced crystalline healing of concrete cracks.” *Cement and Concrete Composites,* vol. 101, pp. 221-231, 2019.

[9] B. Han, W. Sun, and X. Zhang, “Impact of metakaolin on autogenous healing of concrete.” *Construction and Building Materials,* vol. 179, pp. 68-75, 2018.

[10] H. Kalhori, and R. Bagherpour, "Application of carbonate precipitating bacteria for improving properties and repairing of cracks of shortcrete." *Construction and Building Materials,* vol. 148, pp. 249-260, 2017.

[11] N. H. Balam, D. Mostofinejad, and M. Eftekhar, "Effects of bacterial remediation on compressive strength, water absorption, and chloride permeability of lightweight aggregate concrete." *Construction and Building Materials,* vol. 145, pp. 107-116, 2017.

[12] S. Farhadi, and S. Ziadloo, "Self-healing microbial concrete - A review." *Materials Science Forum,* vol. 990, pp. 8-12, 2019.

[13] Y. Jiang, Z. Lv, J. Hu, and C. Yan, "Synergistic effect of metakaolin and Bacillus subtilis on autogenous healing of concrete." *Construction and Building Materials*, vol. 173, pp. 117-126, 2018.

[14] N. Yamasamit, P. Sangkeaw, W. Jitchaijaroen, C. Thongchom, S. Keawsawasvong, and V. Kamchoom, "Effect of Bacillus subtilis on mechanical and self-healing properties in mortar with different crack widths and curing conditions." *Scientific Reports*, vol. 13, no. 1, pp. 7844, 2023.

[15] A. Gharzouni, K. Van Tittelboom, N. De Belie, and W. De Muynck, "Combined effects of metakaolin and Bacillus subtilis on concrete's mechanical properties and biological healing." *Construction and Building Materials,* vol. 277, pp. 122217, 2021.

[16] J. S. Lee, H. K. Kim, and J. K. Song, "Combined effects of metakaolin and *Bacillus subtilis* on the mechanical and durability properties of self-healing concrete." *Construction and Building Materials,* vol. 262, pp.120530, 2022.

[17] G. Dall'Igna, A. Enfedaque, G. Mazzotta, L. Binda, and C. Sbarufatti, "Crack width reduction in self-healing concrete with metakaolin and *Bacillus subtilis*." *Cement and Concrete Composites,* vol. 115, pp. 103740, 2020.

[18] L. Coppola, H. Di Benedetto, L. Torre, R. Cioffi, and F. Fava, "Long-term environmental durability of self-healing concrete with metakaolin and Bacillus subtilis." *Construction and Building Materials,* vol. 293, pp. 123409, 2021.

[19] BS 1881, "Method for Determination of Slump" Part 102:1-10, British Standard Institution, London, 1983.

[20] BS 882, "Specification for Aggregates from Natural Sources for Concrete" British Standard Institution, London, 1992.

[21] BS 1881, "Method for Determination of Compacting Factor." Part 103:1-12, British Standard Institution, London, 1993.

[22] BS 1881, "Method for Determination of the Compressive Strength of Concrete Cores." Part 116, pp. 1-9, British Standard Institution, London, 1983.

[23] BS 1881, "Method for Determination of Flexural Strength." Part 118, pp. 1-12, British Standard Institution, London, 1983.

[24] International Organization for Standardization, "Water quality determination of selected phthalates using GC-MS and GC-MS/MS." ISO 18477, ISO, 2015.

[25] American Standard for Testing and Materials, "Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for use in Concrete." ASTM C618-94;2013; ICS 91.100. 30. American Standard for Testing and Materials, 1994.