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Research Article

Metakaolin-based concrete for marine structures: Performances, chloride binding, and perspectives

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Abstract:

Metakaolin (MK) contains highly reactive alumina, which could be a proper supplementary cementitious material to design low-carbon and durable concrete in marine structures. This review critically examines the characteristics of MK and its effects on cement hydration, mechanical properties, durability, and the chloride-binding capacity. The relatively fine particle size and high volume of reactive contents of silica and alumina enable MK to provide proper filler effects and pozzolanic reactions, forming additional C-A-S-H gels to refine the pore structure of the cementitious matrix. For ternary-blended system, MK could react with calcite to form hemicarboaluminate (Hc) and monocarboaluminate (Mc), while the synergistic use of MK and calcite can enable cement replacement levels of approximately 40-50 wt% while maintaining comparable strength. Appropriate MK incorporation (5 wt% to 10 wt%) can reduce water absorption by up to 38.82% and, in some studies, the carbonation depth could be reduced by 46.1%. Furthermore, MK enhances chloride resistance through physical pore refinement and adsorption, while Hc and Mc promote chemical chloride binding and Friedel's salt formation. These mechanisms demonstrate the potential of MK for durable and low-carbon marine concrete.

Keywords: *Metakaolin; LC3; Durability; Chloride binding; Marine structures*

1. Introduction

Concrete structures have been considered as one of the most popular construction materials, which is expected to undergo significant expansion due to the continuous civilisation. Considering its raw

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materials, cement production accounts for up to 8% of the global greenhouse gas emissions [1-3]. Several studies [4, 5] reported that the cement production would increase to 5.8 billion tons by 2050, posing a significant challenge to the carbon neutrality in the global. As a result, innovative and creative alternatives should be investigated to mitigate the carbon footprint in the construction sector, including high-durable materials or using low-carbon supplementary cementitious materials (SCMs).

SCMs, including biochar [6-9], slag [10, 11], and waste glass powder (WGP) [12, 13], have attracted great attention to partially replacement the cement content for the green and sustainable concrete. Based on a study by Lin et al. [6], 2 wt % fine bamboo biochar could be considered as proper shrinkage-reducing agent for low-carbon cement samples, improving the 28-day strength by 14.6% and reducing the 28-day shrinkage by 16.81%. Ling et al. [14] stated that using up to 3 wt% biochar to replace cement, the chloride resistance was increased by 32% than the biochar-free samples. Tang et al. [15] utilised 30 wt% slag to partially substitute cement, noting that slag-based samples had similar 28-day compressive strength compared to the slag-free samples. Similarly, Li et al. [16] pointed out that the usage of slag as cement replacement did not sacrifice the compressive strength of the samples, but improve the durability properties due to a denser slag-cement matrix. Paul et al. [17] reported that replacing cement by 30 wt% WGP did not lower the compressive strength of the samples with WGP, having a comparable capacity than the reference group. Du et al. [18] observed that samples with 60 wt% WGP exhibited lower 7-day strength when compared to the control group, but at 1 year, WGP-cement samples had similar strength to the WGP-free samples. Overall, using different SCMs exhibited proper improvement in both compressive and durability properties of the SCM-cement composites, also mitigating the carbon emissions for the low-carbon and green concrete designs.

Metakaolin (MK), produced from the high-temperature process of kaolinite ($Al_2Si_2O_5(OH)_4$), could be recognised as a favourable alternative to replace cement content, be attributed to its reactive compound of $Al_2Si_2O_7$ [19-21]. Basically, kaolinite is a white mineral in the naturally available kaolin, where the percentage of kaolinite varies significantly in the kaolin sources across different regions [22]. After dehydration, MK powder is activated containing high percentage of silica and alumina, exhibiting high potential of pozzolanic reactivity [23]. Many studied agreed that [24-26] due to high purity and reactivity of MK powder, the incorporation of MK in concrete could promote better strength development. According to a study by El-Diadamony et al. [27], MK reacted with calcite-based materials to form additional aluminate hydrates, promoting the compactness of the MK-cement matrix to improve the compressive strength. Naresh [28] found that using 10 wt% MK to replace cement led to comparable strengths when compared to MK-free samples. Similarly, Demirel [29] noted that MK powder had relatively fine particle sizes, leading to proper filler effects to promote the hydration and strength development. In addition to MK-cement system, MK is also used as a combination with calcite-based materials for ternary-blended cementing composites. Typically, Campagiorni et al. [30] explained that MK and calcite was used in a ratio of 2:1 as the cement replacement in the ternary blends cementitious composites. They pointed out that the consumption of MK was higher in ternary-blended samples than that in binary-blended system, which was due to better filler effects and more nucleation to promote the cement hydration. In a study by Qin et al. [31], 40 wt% cement was substituted by the combination of MK and calcite, finding that additional hydrates densified the ternary-blended matrix to promote a higher strength

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development than plain cement samples. Antoni et al. [32] also reported that the combination of MK and calcite to replace 45 wt% cement led to a comparable strength than the control samples.

Overall, some studies carried experiments to explore MK's role in the strength development of the MK cementing system [27-30], while some studies [23, 33-35] explored the pozzolanic reactivity of MK as SCMs alternatives, confirming the application of MK powder to establish binary-blended or ternary-blended MK-cement system. Currently, many papers [36-39] have reviewed the effects of MK on the strength development of the cementitious composites, while other studies [40-42] have summarised how MK impacted on the durability properties of the MK-cement composites. However, the review of the potential effects of MK in binding chlorides and long-term behaviours for marine structures is limited. However, considerably less attention has been given to the role of MK in marine concrete, where chloride ingress and binding, wet–dry cycling, coupled chloride–sulphate exposure, and reinforcement corrosion govern long-term structural durability. In particular, the relationships among MK-induced phase evolution, chloride immobilisation, transport resistance, and corrosion initiation remain insufficiently synthesised. Therefore, this review specifically connects the fundamental characteristics of MK with chloride-related deterioration and long-term performance of concrete in marine environments. Therefore, it is worthy conduct a comprehensive review to add more knowledge of MK at different dosages to influence both mechanical and durability properties of the MK-cement composites.

The literature reviewed in this study was primarily retrieved from Scopus, Web of Science, and ScienceDirect using combinations of the keywords 'metakaolin', 'calcined clay', 'cement', 'concrete', 'marine', 'chloride transport', 'chloride binding', 'durability', and 'carbonation'. Peer-reviewed studies relevant to MK-containing cement paste, mortar, concrete, and related binder systems were considered, with particular emphasis on studies reporting hydration, mechanical performance, transport properties, chloride exposure, and long-term durability. Studies with insufficient material or testing information and those outside the scope of cementitious materials were excluded. Paste and mortar studies were primarily used to interpret hydration and phase evolution, whereas concrete studies were prioritised for engineering performance and marine durability.

Overall, this review provides a mechanistic basis for connecting MK characteristics and hydration products with engineering-scale durability in marine environments. Such understanding is important for promoting the reliable use of MK as a low-carbon SCM while maintaining chloride resistance and long-term serviceability of marine concrete structures.

The primary objective of this review was to critically review the chloride-binding capacity and other durability properties of the MK-based concrete in marine environments. Meanwhile, the properties of MK and its effects on the strength development of the samples were thoroughly investigated. The impact of MK powder on the durability properties of samples with MK was reviewed, including water permeability, shrinkage, and carbonation. In addition, other characteristics of MK-based composites, such as effects on fresh concrete were also discussed.

2. MK properties

Metakaolin is normally considered as a type of pozzolan with specific ability to react with portlandite or calcite, being a favourable raw material to partially replace cement. After being

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calcined in high temperature of 600 – 800 degrees, kaolin was converted to MK, containing 1:1 type of phyllosilicate and 2:1 phyllosilicate [43, 44]. As shown in Fig. 1a, alumina was bonded with oxygen or hydroxyl, where silicate was mainly located in the next layer. Both 1:1 and 2:1 types of the metakaolin are formed in sandwich-like shapes with multiple layers. In the study by Al-Jabri and Shoukry [45], the image in Scanned electron microscopy (SEM) evidenced the sheet-shape of the MK particles. Fig. 1b indicated that MK powder had irregular shape, formed by multiple layers. In terms of MK's size, the SEM image revealed that MK particles have relatively fine size, which is in both microscale and nanoscale [46].

Ndahirwa et al. [40] reported that high-purity MK had a specific surface area in a range of 10 – 20 m^2/g, where its median particle size was found between 1.3 to 3 μm. Boakye et al. [47] added that the calcination process could affect the formation of MK, leading to the differences in the specific surface area. For instance, they reported that the surface area of MK was reduced from 18.6 m^2/g to 12.6 m^2/g when the temperature raised from 700 to 800 degree. Apparently, this size of fineness exhibits small size than that of the cement grains, being around 10 μm, having a favourable filler effect in the cementitious matrix. Combining these aspects, MK could be considered to be a very suitable alternative to partially replace cement for the sustainable concrete.

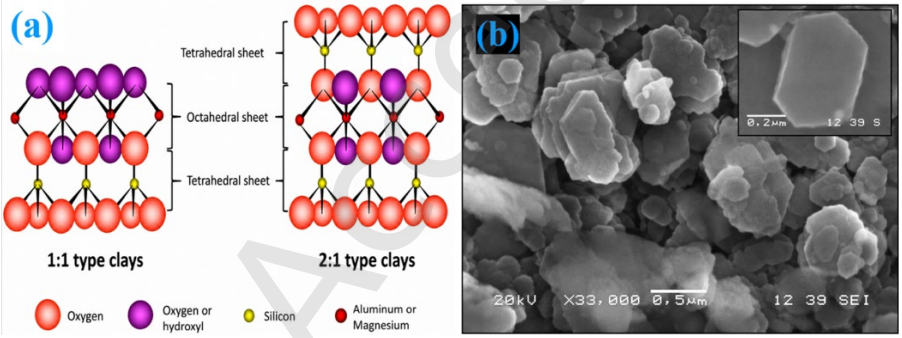


Fig. 1 Metakaolin structure: (a) MK layer [44]; (b) MK SEM [45]

Table 1 presents the chemical compositions of MK from different regions. Typically, MK particles contain enormous amounts of Al_2O_3 and SiO_2, in which these two compositions account for 90% of the MK content. However, it should be noted that due to the location and mineral variances, some MK powders [48, 49] exhibit lower content of silica, locating in Nigeria and Algeria. The combination of silica and alumina allows MK to be a proper alternative for cement replacement with high level of reactivity. Adesanya and Raheem [50] mentioned that due to high content of Al_2O_3 and SiO_2, metakaolin could be considered as a highly reactive pozzolan materials, which could react with portlandite or calcite to form additional hydrates, promoting the secondary hydration development. As a result, the MK-cement composites could have a denser microstructure than the traditional cementing matrix. It should be pointed out that MK does not contain sufficient CaO, which is a major difference to other SCMs, such as slag or fly ash, while it has the ability to react with calcium-based hydrates to promote the formation of calcium aluminate hydrates in the long-term. As shown in the XRD analysis by El-Diadamony [27] in Fig.2, the metakaolin had significant amount of silica, being a favourable factor as SCMs.

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Overmann et al. [51] pointed out that chemically speaking, rich content of Al_2O_3 and SiO_2 (>30 wt%) in MK could highlight its high reactivity, where the presence of 5-coordinated aluminium (AlO_5) was the main contributor. Some studies [38, 52] mentioned that this phenomenon was highly dependent on the production process, where the calcination temperature and methodology could affect the formation of 5-coordinated aluminium, thereby impacting on the reactivity of the MK powder. Overall, MK has limited availability of other compositions, lowering in K_2O, Na_2O, and MgO, while the content of Fe_2O_3 is also dependent on the location of the raw kaolin.

Table 1. Chemical compositions of MK powder.

Refs.	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	LOI
[53]	78.93	0.56	12.41	4.54	0.01	0.89	0.19	2.47
[54]	53.03	0.04	35.63	1.81	0.57	1.88	0.04	7
[55]	53.01	0.02	43.78	0.43	0.03	0.19	0.23	2.31
[56]	55.31	0.85	41.55	0.12	0.04	0.09	0.05	1.99
[57]	52.9	0.26	42.8	0.51	0.84	0.12	0.05	2.52
[49]	38.32	0.48	33.23	14.63	0.01	1.64	0.02	11.67
[48]	41.08	3.01	52.86	1.23	0.03	0.12	0.01	1.66

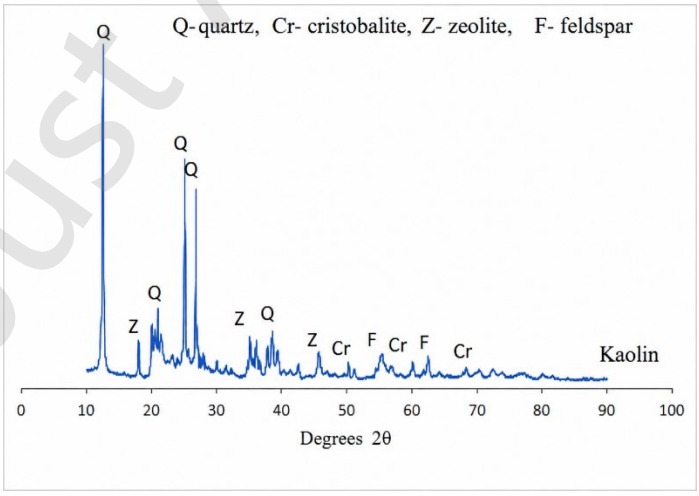


Fig. 2. XRD pattern of MK powder [27]

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3. Effects of MK on concrete hydration and strength

As a typical cement replacement material, MK could be used from 20 wt% to 40 wt% in the MK-cement composites. However, it is important to understand how MK would affect the properties of both fresh and hardened cementitious composites, the following sections will discuss the effects of MK in different cementing system.

3.1 Hydration development

Ghazy et al. [42] mentioned that the application of MK in the cementing system led to an enhancement in the hydration development, due to the reactivity of alumina to induce the pozzolanic reactions. Sundararajan [58] added that after portlandite formed in the early age, it would further reacted with alumina to form C-A-S-H, reducing the timeframe of both initial setting and final setting times. In addition, due to high-level cement replacement, the addition of water-reducing agent would affect the hydration development of MK-cement system [59]. Using only MK as cement replacement, Li and Ding [60] found that 10 wt% MK promoted a reduction of 26% and 36% in initial and final setting time respectively. However, when MK is used with calcite-based materials, the reaction between calcite and MK powder would lead to additional intensified formation of aluminate peak [61, 62], such as hemicarboaluminate (Hc) and monocarboaluminate (Mc), further improving the cement hydration.

As shown in Fig. 3, MK+LS system exhibited a significant peaks of aluminate formation and Hc and Mc formations, indicating the further densification of the matrix [63]. Comparing with the traditional paste having the alite and belite dissolution as the main hydration peak, MK-LS system or limestone-calcined clay system has second and third peaks (Fig. 3), promoting the compactness of the ternary blended system to resist against the water ingress, having a good agreement with other studies [64, 65]. However, Zhan et al. [57] investigated the hydration development of MK-LS-cement system under ultra-low water to binder ratio of 0.16, reporting that the presence of Polycarboxylate ether (PCE)-based superplasticiser significantly affected the hydration dynamics. Due to addition of 4 wt% PCE, small delay is found in samples with water to binder ratio of 0.16 when comparing to that with normal water to binder ratio of 0.4 – 0.5. The reason is that PCE particles would attract calcium ions to improve the formation of portlandite and CSH gels. In other words, PCE-based water reducing agent could activate the pozzolanic reaction of MK with portlandite and calcite, forming additional C-A-S-H and carboaluminates (Hc and Mc) to improve the density of the ternary-blended system. In addition to experimental characterisation, coupled kinetic–thermodynamic modelling provides a useful approach to predict the hydration of limestone–calcined kaolinitic clay systems. Yu et al. [66] linked calcined-clay reactivity, including R^3-test results, with hydration kinetics and thermodynamic phase assemblages for clays containing different kaolinite contents. Such modelling provides a quantitative framework for evaluating how raw-material variability influences the hydration and phase evolution of MK/limestone-containing binders.

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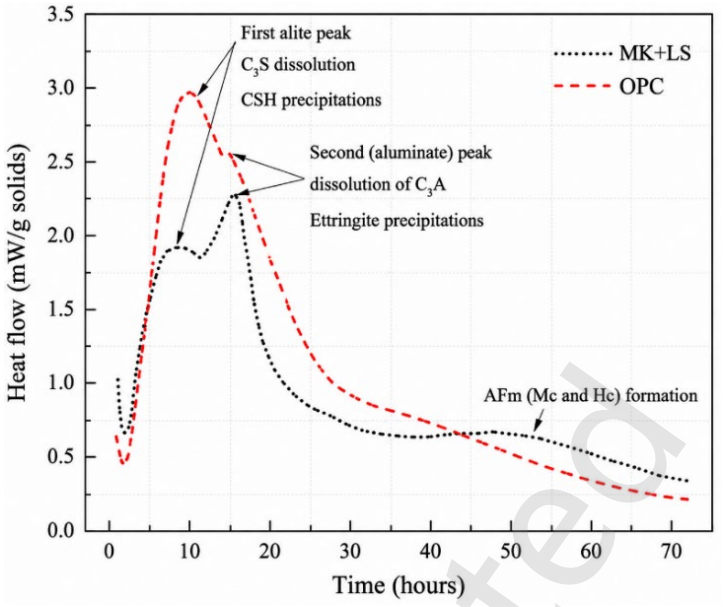


Fig. 3. Comparison of hydration development of samples with and without MK [63].

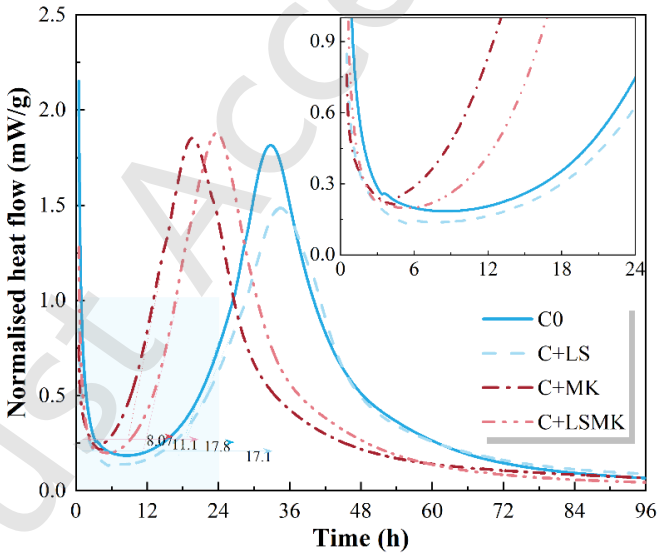


Fig. 4. Normalised heat flow comparison for different pastes [57]

3.2 Workability

Considering the properties of MK, including fine particle size, angular shape, and relatively high specific surface area, up to 40 wt% of MK would lower the workability of the MK-cement slurry [67], requiring additional free water or use of water-reducing agent. Nicolas et al. [68] found that since the high-temperature process would lead to degradation of crystals to the amorphous phases, the increase of the surface area and shape transformation led to an increase of the water consumption and reduce in the slump of the MK-cement composites. In terms of flash calcination, MK powder

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would have up to 15 wt% of the particles with the spherical shapes, reducing the water consumption and increasing the workability of the MK-cement mix [69]. In addition, the content and distribution of alumina also affect the workability of the MK-cement system. Ahmad et al. [70] observed that when more alumina was found in MK powder, it posed a higher demand for free water, being attributed to the activation of pozzolanic reaction consuming portlandite to form additional C-A-S-H. Geu et al. [71] stated that the calcination temperature played an important role in affecting the reactivity of MK, where MK produced with temperature higher than 800 degrees required less water due to low reactivity. As a result, the calcination temperature of MK powder was indirectly proportional to the workability of the MK-cement composites.

3.3 Compressive strength

In terms of compressive strength, due to the relatively fine size, MK addition promotes a favourable filler effect, improving the strength development. Pillay et al. carried out experiments by replacing cement with up to 20 wt% MK, and reporting that up to 10 wt% biochar could promote the compressive strength development of MK-cement samples. As presented in Fig. 5 [72], 5 to 10 wt% MK could promote higher strength development of MK-based samples than the MK-free samples, in particular, 5 wt% MK led to the highest 28-day compressive strength. One interpretation is that MK particles provide proper filler effects, and part of MK powder reacts with portlandite to form additional CSH gels, improving the strength capacity when comparing to the control group. It is clear that 10 wt% MK led to a denser microstructure in MK-cement matrix with small volume of pores (Fig. 6) [72]. Similarly, Khater [73] mentioned that the pozzolanic reaction between MK and portlandite contributed to additional strength development, leading to a higher compressive capacity, being consistent with other studies [74-76].

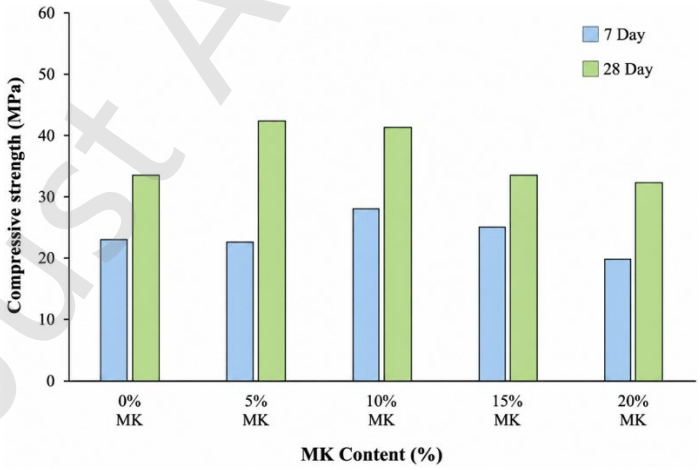


Fig.5. Effects of MK on the compressive strength of the samples [72]

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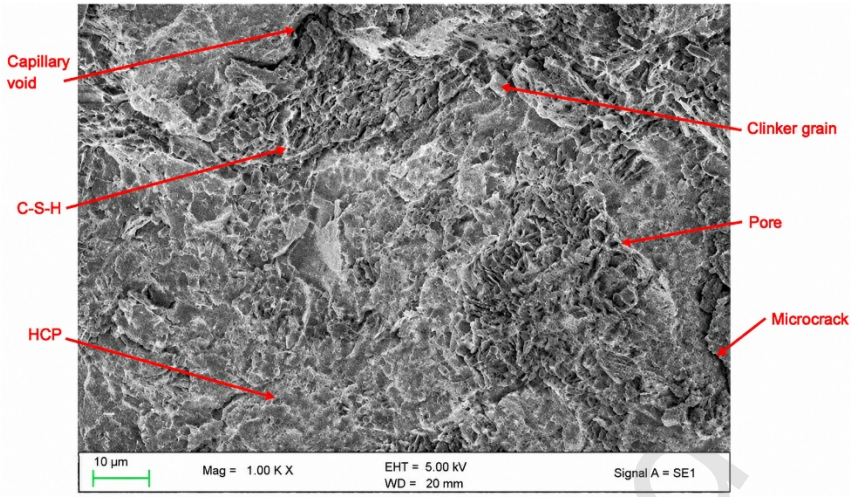


Fig. 6. A typical SEM image of samples with 10 wt% MK [72]

For combination of MK and calcite, the replacement dosage could be higher than using MK alone. In a study by Zhan et al. [57], 20 wt% cement was replaced by MK and calcite, finding that ternary-blended samples exhibited comparable 3-day strengths to the control group, while long-term pozzolanic reaction led to additional strength development. Sharma et al. [61] reported that for 28-day compressive strength and long-term strength, MK or calcined clay could be used with calcite to replace 30 wt% cement without lowering the strength, being attributed to the pozzolanic reaction and formation of carboaluminates. Some studies [77, 78] observed that when the cement replacement raised to up to 50 wt%, the ternary-blended samples displayed comparable strengths with the reference group, bolstered by the additional formation of hydrates (Hc and Mc) to refine the porosity of the matrix. As a result, the compressive strength of the samples is improved. However, some studies [79-81] argued that the calcination process, water to binder ratio, or pozzolan contents impacted on the compressive strength development of the samples. This is due to the variances in the particle shapes, particle formation, and the particle arrangement of MK powder, leading to different contributions to the strength gain of MK-cement composites. Overall, it is agreed that small amount of MK could lead to higher strength gain, while the combination of MK and calcite could be used up to 40 wt% to 50 wt% as cement replacement.

It should be emphasised that the favourable MK replacement level is system-dependent rather than universal, as cement chemistry, MK reactivity and fineness, water-to-binder ratio, curing age and temperature, exposure conditions, and the targeted property can substantially influence performance. Bu et al. [82] further demonstrated this dependency under high-temperature oil-well conditions: high MK contents reduced early strength under some conditions, whereas 40–60 wt% MK maintained favourable performance at 150 °C and above. Although these conditions differ from conventional marine exposure, the study provides a useful boundary case against generalising a single optimum MK dosage.

3.4 Tensile strength

In a study by Saand et al. [83], up to 20 wt% MK was used as cement substitute, and they found that unlike the compressive strength of the MK-cement composites, the improvement in the tensile

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strength was relatively small (Fig. 7). One possible interpretation is that although fine-size MK particles provide filler effects to improve the compactness of the MK-cement matrix, the brittle nature of the cementing composites does not change. As a result, the strength increase is minor. According to Fig. 7, up to 15 wt% MK as cement replacement does not lower the tensile strength of the samples with MK addition, while samples with 20 wt% MK had a slight small tensile strength than that of MK-free samples.

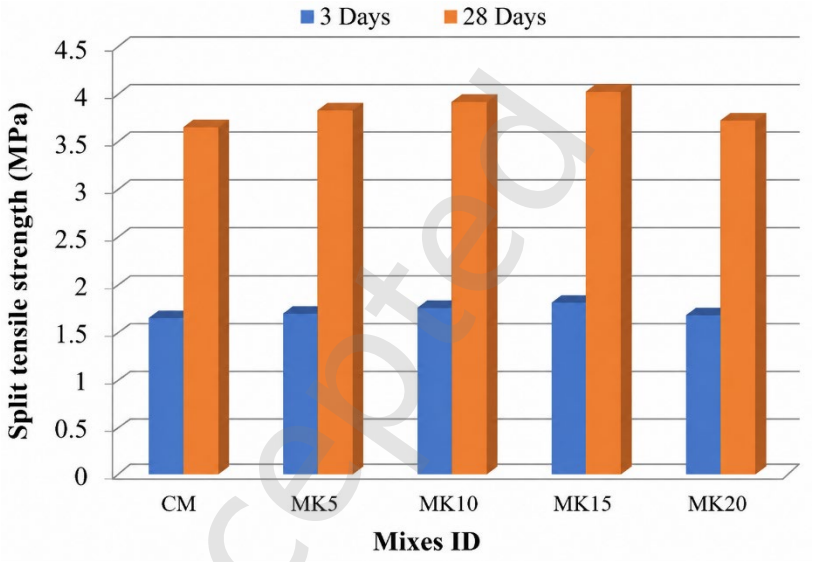


Fig. 7. Tensile strength of samples with MK [83]

Singh et al. [84] agreed that although possible pozzolanic reactions and proper filler effect allowed MK to induce additional hydration products, it did not mitigate the inevitable brittle nature of the matrix, being vulnerable to shear forces. In addition, Salimi et al. [85] observed that the presence of excessive content of low-reactivity MK (15 wt% to 20 wt%) created weak points in the MK-cement matrix, leading to lower resistance against the tensile loads. Overall, the presence of MK does not significantly improve the tensile capacity, while a denser microstructure could slightly improve the tensile strength of the MK-cement composite.

3.5 Flexural strength

Similar to findings in tensile strength analysis, the incorporation of MK in the cementing system does not improve the flexural capacity significantly. Fig. 8 depicts the potential effects of MK in the 28-day flexural strengths of different samples [86]. Muduli et al. [86] observed that up to 20 wt% MK powder as cement replacement did not change the strength development of the MK-cement composites in a big range. The reason could be that even though fine-size MK powder refines the microstructure of the MK-cement composites, the brittle nature of the MK-cement matrix is not changed. As a result, combining filler effects and pozzolanic reaction, the flexural strength of MK-cement composites is not greatly improved.

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Some studies [86, 87] reported that MK powders could improve the binding between the recycled aggregates and the cementitious matrix, enhancing the structural strength. They stated that MK powder acted as a kind of bridge, improving the ITZ between the aggregates and the matrix, while the flexural strength was slightly improved. This may be due to fine-size MK particles fill in the voids between recycled aggregates and the surrounding matrix, while further pozzolanic reaction could also provide stronger bonding. Singh et al. [88] explained that due to variance of demolition source of recycled concrete, the potential interaction of recycled aggregates and MK remained differently. Since MK could react with both portlandite or calcite to form different hydrates, recycled aggregates with various compositions would provide different bonding to the MK. However, although the stronger bonding is established, the brittle nature still poses less strength increment in flexural capacity of MK-cement composites.

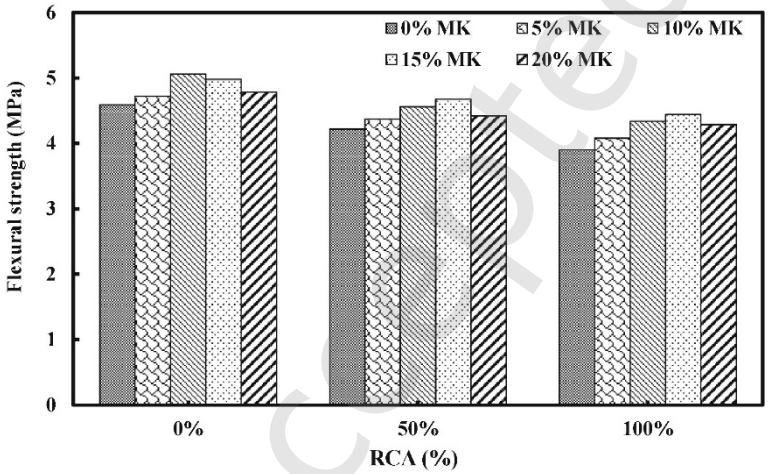


Fig. 8 Flexural strength of samples with and without MK [86]

In general, the presence of MK has both physical and chemical effects on the strength development of the samples [77, 78, 80, 83, 86, 88]. First of all, in terms of physical effects, MK powder normally has a relative finer size when compared to that of the cement, having a great potential for filler effects and offering more nucleation sites for the hydration development. Li et al. [89] reported that when incorporating MK in the cementitious matrix, finer-size MK particles initially filled the pores and voids in the matrix, and the activation of pozzolanic reactions further densified the matrix, leading to the reduction of porosity. As shown in Fig. 9, the cumulative pore volume of samples without MK is higher than those of samples with MK [89]. The addition of MK could provide desirable filler effects to the cementitious matrix, while the pore volume is reduced to the porosity refinement in MK-cement system, which is beneficial to improve the strength development of the samples. Lazaro et al. [44] added that considering the phyllosilicate structure of MK particles, the silicate layer played an important role in the strength development of MK-cement matrix. Medhigbodo et al. [90] believed that the relatively large surface area of MK particles also provide more nucleation sizes of the hydration products formations, promoting the cement hydration process to improve the early-age strength gain when compared to the reference group. Some studies [44, 83, 86, 90] supported that if the MK powder had more content of nanoscale particles, the filler effects would be superior to the microscale MK powder, highlighting the significance of the

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nanoparticles in facilitating the strength development of the cementing matrix. Overall, fine-size MK particles provide advantages in strength development in physical aspects, including filler effects and large surface area for more nucleations.

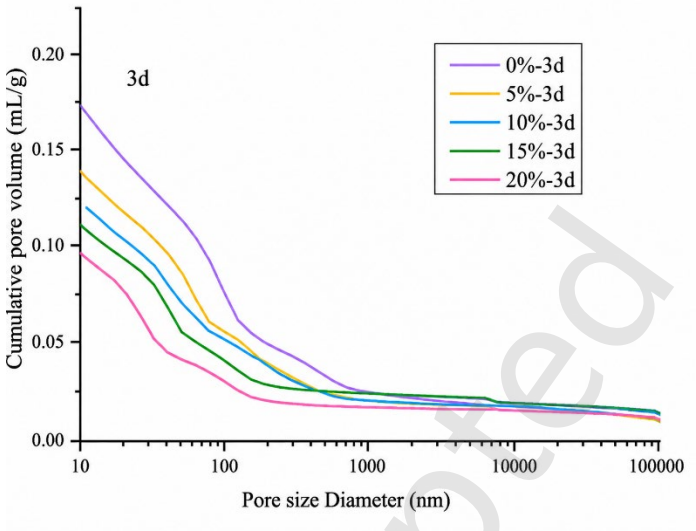


Fig. 9. Cumulative pore volume of samples with and without MK [89]

Considering the chemical effects of the strength development, it could be mainly two types: reaction between MK and portlandite to form additional C-A-S-H gels and reaction between MK and calcite-based materials to form Hc and Mc [50, 58, 61, 62]. For pozzolanic reactions, hydrated products of portlandite are further reacted with alumina in MK powder, forming additional C-A-S-H gels to fill in the existing pores of the matrix. As a result, a denser microstructure is formed to resist the loadings. Based on Fig. 10, the SEM images reveal that addition of MK could denser the MK-cement matrix [91]. Luo et al. [91] observed that MK powder reacted with portlandite to form additional C-A-S-H gels, providing better bonding in the MK-cement matrix when compared to that of the MK-free matrix. Thus, the mechanical properties of the samples are improved. On the other hand, in ternary-blended system, MK could also react with calcite to form Hc and Mc, in which the existing porosity could be refined to reduce its volume. To sum up, the chemical effects of MK in the strength development are mainly the pozzolanic reactions and reaction between MK and calcite to produce additional hydrates in densifying the existing MK-cement matrix.

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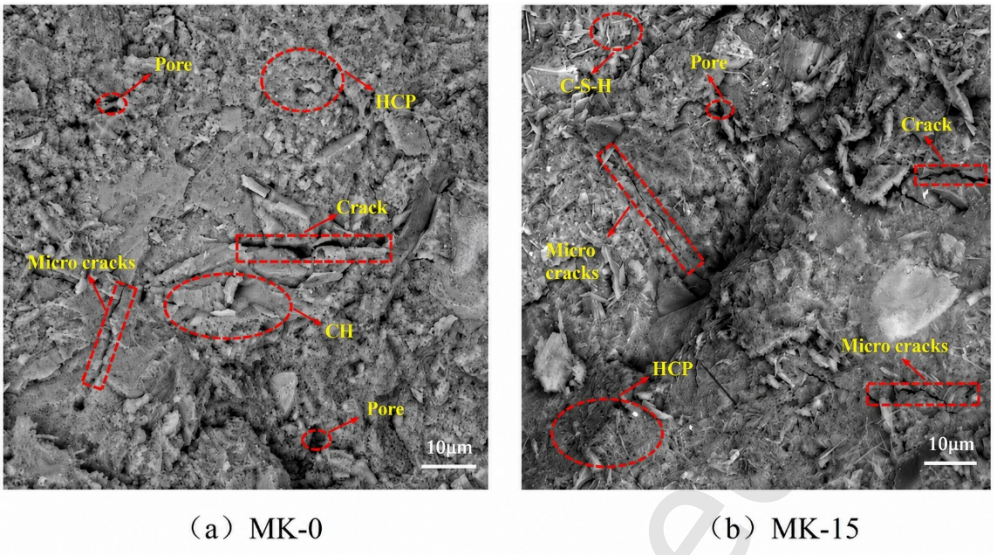


Fig. 10 SEM images analysis [91].

4. Effects of MK on concrete durability

Since MK widely used as a supplementary cementitious material and can replace cement at relatively high levels, typically up to 40–50 wt% in LC3 system of up to 20 wt% in MK-cement system. Such high-volume cement replacement could greatly influence the hydration process, porosity, and matrix density of the MK-cement composites, thereby impact the long-term durability properties of the samples. In particular, since the addition of MK could promote pozzolanic reactions to induce additional formation of CSH gels in densifying the matrix, it shows good potential in improving the durability properties. As a result, a systematic review of durability performances of MK-cement composites should be conducted.

4.1 Permeability

Permeability indicates the ability of the hardened samples to resist water penetration when immersed in the water or other solutions, where it could be used to reflect the porosity and potential reactions with the water molecules. In generally, the water absorption of a durable concrete sample should be in the range of 4 – 6%. Some studies [77, 92, 93] reported that MK application could improve the pore structures in the MK-cement matrix, leading to changes in its water penetration rate. Mas and Kurbetci [94] observed that MK could react with the existing portlandite to form additional CSH gels, improving the early-age density of the cementitious matrix. Bansal et al. [95] used 10 wt% MK as the cement replacement, finding that up to 38.82% reduction on water absorption could be achieved when compared to that of MK-free samples. They pointed out that MK addition facilitated a denser MK-cement matrix limiting the water access to the deep matrix.

Joshaghani et al. [96] explained that the distribution of pores and density of ITZ affected the resistance or susceptibility of samples against water and aggressive-ion ingress, typically, when the network of cement matrix was more accessible, the matrix would experience higher degree of water penetration. Keerio et al. [97] found that 15 wt% MK was an optimal dosage to limit the access of

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water molecules, since fine-size MK could promote a better microstructures when compared to that of the MK-free samples Fig. 11. Shekarchi et al. [98] added that up to 50 wt% and 37% reduction were found in water permeability and gas permeability respectively. However, it should be noted that further dosage increment would lead to higher water penetration depth. One possible reason is that excessive amount of MK would interfere with the hydration development, where cement dilution leads to some weak areas for water to penetrate. If the cement hydration is negatively affected, it would create more accessible channels in the capillary networks, lowering the compactness of the matrix. As a result, the incorporation of MK as cement replacement should be limited for a better performance against water penetration.

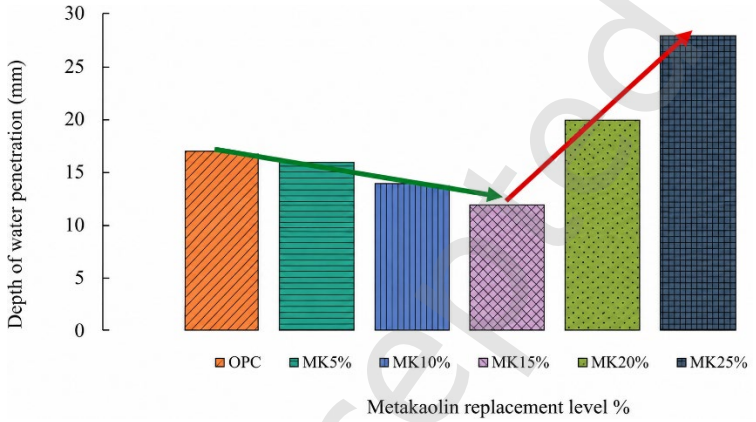


Fig. 11. Permeability comparisons of different samples [97]

4.2 Sulphate attack

Sulphate attack has been a major issue affecting the durability properties of the concrete structures exposed to sulphate-rich solutions or environments. The concern is that sulphate ions could react with hydration products to form expansive phases (ettringite and gypsum), where excessive formations for sulphate-based salts would result in sample expansion and potential cracking, lowering the structural resilience of the concrete samples. In order to express the resistance against sulphate attack of the MK-cement samples, the change in sample mass and strength could be used to determine the degradation of samples in the aggressive environment. Some studies [99-101] pointed out that pozzolanic reaction of MK exhibited a proper improvement against harmful ingress of sulphate ions. Shi et al. [99] found that the ternary-blended system displayed minor length change against sulphate solution ingress after 2-year exposure (Fig. 12), showing desirable performance of MK-calcite-cement system in limiting the access of sulphate and water molecules.

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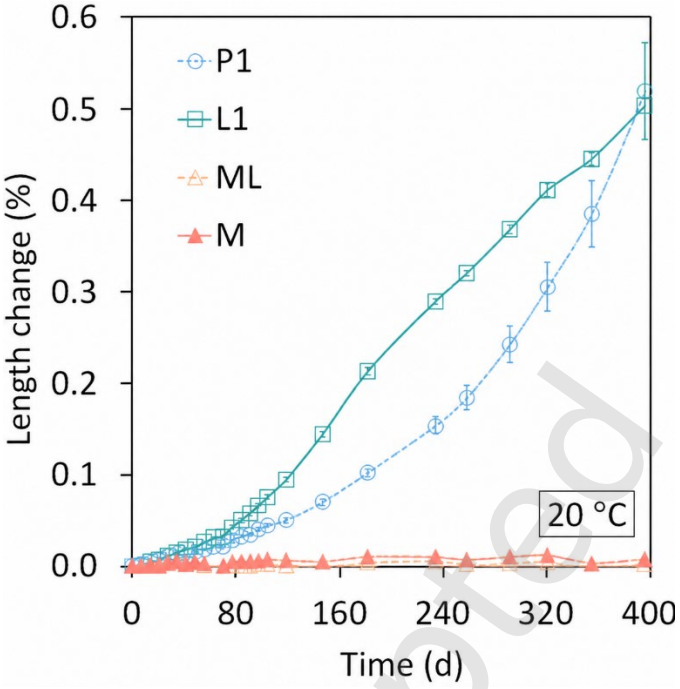


Fig. 12. Length change of samples exposed to sulphate solution

Sharma et al. [102] used up to 20 wt% MK as the cement replacement for 120-day sulphate immersion, and observing that 10 wt% MK addition led to the lowest mass gain (0.16%) when compared to that of the control (0.45%), highlighting the appropriate influence of MK powder in refining the pore structure of the MK-cement composites. According to a study by Song et al. [103], MK particles could initially refined the pore structures and then react with portlandite to further improve the compactness of the matrix, mitigating the access of water and sulphate ions into the deeper cementitious matrix. Other studies [104, 105] added that the mitigation of capillary pore development was the main fact to improve the resistance against sulphate attack, where the denser microstructure not only provided higher strengths, but also formed a protective layer to the deeper matrix.

4.3 Shrinkage deformation

Shrinkage deformation is a complex long-term problem of the concrete samples, governed by time-dependent changes in temperature and moisture. This volume stability concern could lead to minor cracks in the early age [106], causing unexpected cracking development, which could poses the structure to further issues, such as rebar erosion and damage to deeper matrix. After the casting, the moisture will escape from the matrix, leading to increase in self-desiccation and imbalance in the internal forces. As a result, the drying shrinkage is a major issue for most of the concrete samples.

As shown in Fig. 13, Salimi et al. [85] used different MK dosage as the cement replacement to test the shrinkage deformation. They found that at low water to binder ratio (0.34-0.4), up to 5 wt% MK could be used as the cement replacement without increasing the shrinkage deformation up to 60 days of exposure. However, as shown in Fig. 13, for water to binder ratio of 0.45, due to higher

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availability of free water, higher dosage of MK could be used as the cement replacement. The reason could be that due to excessive presence of MK powder in the matrix, it negatively impacts on the pore refinement, leading to higher accessible network to water evaporation. As a result, the drying shrinkage of the MK-cement composites is higher than the control. Similarly, Elsafty et al. [107] observed that 5 to 10 wt% MK could be an optimal dosage to limit the shrinkage deflection of MK-cement samples. They suggested that excessive presence of MK also demanded higher volume of free water, negatively increasing the internal forces to increase the shrinkage deformations of the samples.

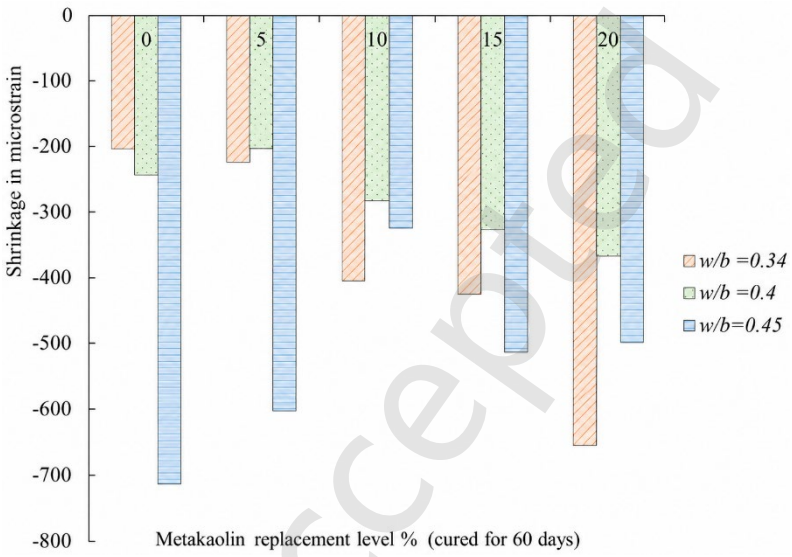


Fig. 13 shrinkage comparisons for samples with and without MK [85]

4.4 Carbonation

Carbonation is another long-term durability issue of the concrete exposed to the air, mainly involving the penetration of free carbon dioxide into the matrix. It could react with the hydration products to form calcite, lowering the alkalinity of the pore solution and pH level in the cementitious matrix. This phenomenon would then lead to de-passivation and subsequent rebar corrosion, resulting in loss of the structural strengths of the concrete samples [108]. Li et al. [109] summarised the factors affected the carbonation of the concrete samples (Fig. 14). They noted that the environmental factors such as air humidity and surrounding conditions had primary impact on the carbonation, since they could promote the carbon dioxide ingress to the concrete. Another factor contains mainly the concrete types, porosity of the composites, and the SCMs as the additives, in which a denser microstructure could limit the access of water and carbon dioxide, improving the resistance against the carbonation.

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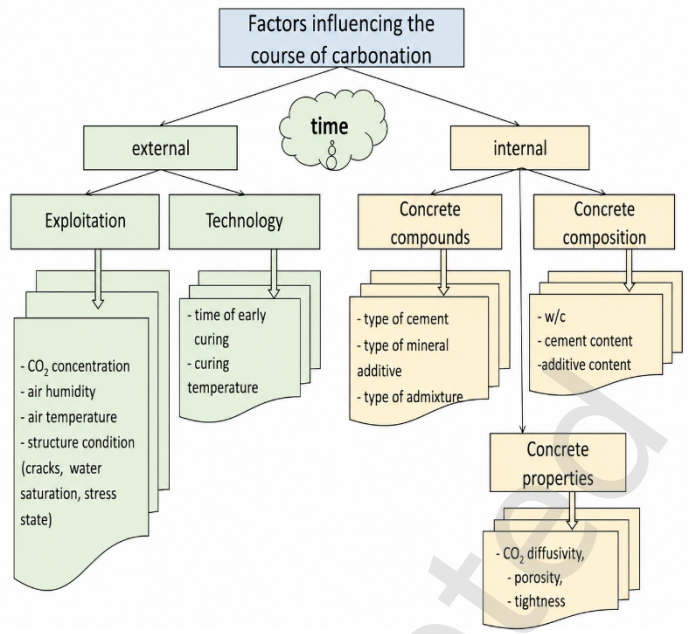


Fig. 14 Carbonation process in the concrete structures [109]

Ayub et al. [110] discussed that in the presence of MK powder in the matrix, the porosity of the MK-cement composite was refined to improve carbonation resistance due to pozzolanic reactions and proper filler effects. Furthermore, they pointed out that another benefit of MK addition was that MK consumed portlandite in the cementitious matrix, lowering the potential reactions between carbon dioxide and portlandite. Ashish et al. [111] reported that 10 wt% MK as cement replacement could lead to a reduction of 46.1% in the carbonation depth when compared to that of the MK-free samples. They argued that the favourable improvement could be due to the transition of portlandite to CSH gels in refining the exiting pore structures, mitigating the penetration of carbon dioxide, having a good agreement with other studies [112, 113]. However, due to the various reactivity of the MK powder, the effects on carbonation depth are different. Kim et al. [87] reported that 10 wt% MK addition led to an increase of 30% in the carbonation depth than the reference group at 28 days. The reason could be that their MK has relatively low reactivity, where the portlandite is not consumed to further refine the porosity to improve the carbonation depth.

These contrasting results demonstrate that MK does not universally improve carbonation resistance. The resulting performance depends on the balance between pore refinement and portlandite consumption, together with MK fineness, reactivity, replacement level, curing conditions, and water-to-binder ratio.

It should also be distinguished that carbonation during structural service and concrete recarbonation from a life-cycle perspective represent different considerations. In reinforced marine concrete, carbonation can reduce pore-solution alkalinity and promote reinforcement depassivation, thereby increasing corrosion risk. Conversely, concrete can reabsorb atmospheric CO2 during service and particularly after demolition, crushing, stockpiling, recycling, and secondary use. Patrisia et al. [114] proposed a life-cycle framework for quantifying such recarbonation potential.

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However, MK-specific CO2 uptake under marine exposure remains insufficiently quantified and should be further investigated rather than directly extrapolated from conventional concrete.

Overall, by combining the afore-mentioned literatures, the effects of MK on the MK-cement composites could be governed by few factors: First of all, MK particles could react with portlandite to process pozzolanic reactions to reduce the porosity of the matrix, leading to a denser microstructure in resisting the water and other ions ingress (Fig. 15). In the presence of calcite, MK could further react with calcite to form Hc and Mc, which could improve the compactness of the exiting matrix, being a favourable role in refining the capillary structures. Secondly, due to finer-size MK as the cement replacement, the early age hydration is improved due to filler effects and more nucleation sizes. This fact could promote the strength gain and proper matrix development. Considering these factors, the MK-cement composites have better resistance against permeability, sulphate attack, shrinkage deformation, and carbonation.

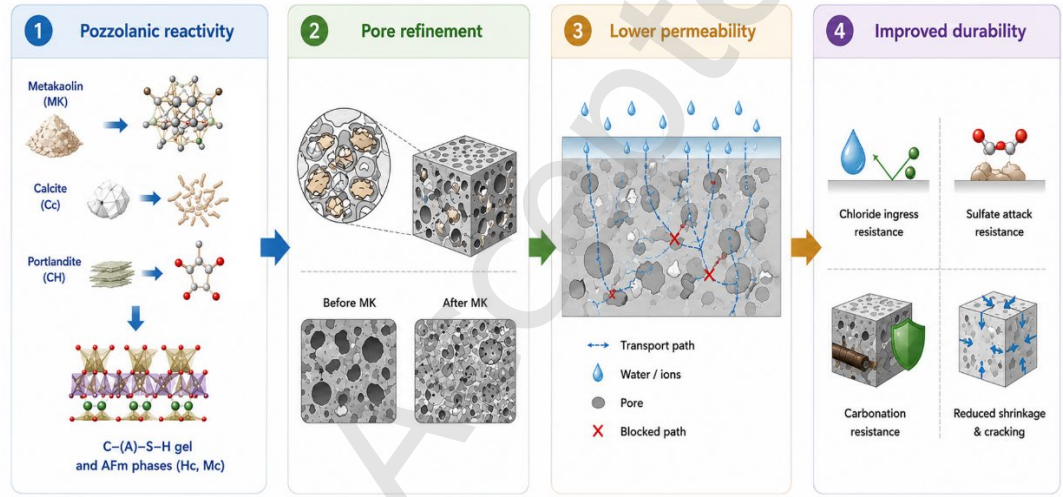


Fig. 15. Summary of effects of MK in concrete structures

However, it should be noted that the performance of MK-cement composites is highly dependent on its particle size and the reactivity of the MK powder. Finer-size MK could have better regulation against the durability concerns, while coarse-size MK powder may interfere with the strength and hydration development. The reactivity of MK also governs the activation of the pozzolanic reactions and porosity refinement. Thus, when analysing the benefits of MK in the concrete, the particle size and reactivity should be considered. Interfacial performance of MK-based materials requires further investigation for marine repair applications. Alkali-activated MK systems have shown potential for interface consolidation and fluid sealing in other aggressive environments [115]. Although these conditions differ from marine exposure, future studies should evaluate bond retention, interface integrity, and fluid tightness of MK-based repair layers, grouts, and construction joints under chloride exposure and repeated wet–dry cycles.

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5. Effects of MK on chloride-binding capacity

Another important factor of concrete structures in marine environment is the chloride-binding capacity, which is a long-term durability concern since continuous exposure to chloride ions in the seawater, promoting the chloride-ion penetration [116]. Normally, chloride ions could be adsorbed via both physical and chemical binding, mitigating or delaying their penetration to the rebar inside the matrix. By chloride binding, this process could ensure the steel passivation and eliminate the chloride ingress, thereby reducing the occurrence of expansion-induced cracking and deterioration [117]. As a result, improvement on chloride-binding capacity seems to be an effective way to ensure the durability resilience of marine structures.

Chloride-related performance of marine concrete should be distinguished in terms of chloride transport, penetration, and binding. Chloride transport and penetration describe the movement and ingress of chloride ions through the pore network and are strongly influenced by matrix porosity and connectivity. In contrast, chloride binding refers to the immobilisation of chloride ions within the cementitious matrix. Physically bound chloride is mainly associated with surface adsorption on hydration products, whereas chemical binding involves reactions with Al-bearing phases and the formation of chloride-containing phases such as Friedel's salt. Free chloride in the pore solution is directly relevant to reinforcement depassivation, whereas total chloride includes both free and bound fractions. Accordingly, a reduction in chloride penetration caused by pore refinement should not be directly interpreted as an increase in chloride-binding capacity.

Dhinakaran et al. [118] reported that using up to 15 wt% MK as the cement replacement, the chloride penetration of the samples with MK was lower than that of the MK-free samples. The reason could be that MK powder refined the porosity of the matrix lowering the potential of chloride ingress. Similarly Babaahmadi et al. [119] observed that samples with 15 wt% MK exhibited higher chloride-binding capacity when compared to the MK-free samples. However, Shi et al. [93] used MK and calcite to replace up to 35 wt% cement, and observing that samples with MK had lower chloride penetration against the reference group Fig. 16. They reported that MK reacted with portlandite to improve the density of the matrix, while MK also reacted with calcite to form Hc and Mc, which had the ability to react with chloride ions to form Friedel's salt, binding the chloride ions chemically. Ipavec et al. [120] agreed that in the presence of calcite, the samples with MK could exhibit a higher chloride-binding capacity when compared to samples with only MK, highlighting the importance of Hc and Mc to adsorb chloride ions. In particular, since Hc and Mc are porous structures, they could also adsorb the chloride physically.

Direct comparison of reported chloride-binding capacities should nevertheless be made cautiously because water-to-binder ratio, MK dosage, curing age, chloride concentration, exposure method, and analytical technique vary considerably among studies. These variables also affect whether the reported result represents transport resistance, free chloride, total chloride, or true binding capacity.

Table 2. Comparison of representative studies related to chloride transport and binding in MK-containing cementitious systems.

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Reference	MK/binder system	MK level	Exposure / test focus	Chloride metric	Major finding
Dhinakaran et al. [118]	MK-cement	Up to 15 wt%	Chloride penetration	Transport / penetration	MK reduced chloride penetration relative to the control.
Babaahmadi et al. [119]	MK-cement	15 wt%	Chloride exposure	Binding capacity	MK increased reported chloride-binding capacity.
Shi et al. [93]	MK + calcite-cement	Up to 35 wt% total replacement	Chloride penetration/binding	Transport + chemical binding	Pore refinement and Hc/Mc formation contributed to lower penetration and chloride immobilisation.
Ipavec et al. [120]	MK + calcite system	Reported ternary system	Chloride binding	Chemical binding	Calcite-containing MK systems promoted chloride binding through Al-bearing phases.

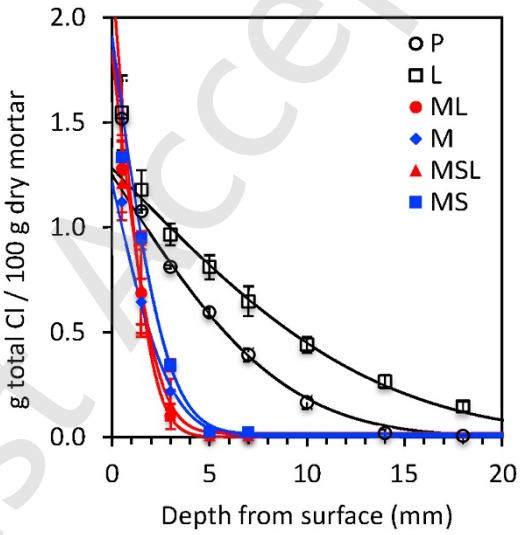


Fig. 16 Total chloride profiles in samples with and without MK [93]

Overall, based on aforementioned literatures, MK plays a significant role in regulating the chloride-binding capacity of the cementitious composites. The high reactivity phases such as alumina allow MK to process secondary hydration and pore structure modification. In the presence of MK in the cementitious matrix, MK initially react with portlandite to induce pozzolanic reactions, generating more CSH gels to refine a denser microstructure (**Fig. 17**). Meanwhile MK powders also react with calcite materials to form Hc an Mc, which create more reservoirs for storing chloride ions. These two phases subsequently improve the chloride immobilisation through both physical and chemical binding as shown in **Fig. 17.**

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Physical binding is associated with the improved pore structure, which is a result from pozzolanic reaction and reaction between MK and calcite. The chloride could be adsorbed on the surfaces of different hydration products, limiting the chloride transport into the deeper microstructure, thus MK addition could reduce the chloride-ion penetration and secure the chlorides in the pore solution. As depicted in Fig. 17, the chemical binding involves the further reaction between Hc and Mc, which are the Al-bearing phases. Chloride ions could act as an exchange with the interlayer structure of Hc or Mc, resulting in chemical binding of chloride ions and Hc or Mc. The new phase is typically identified as Friedel's salt.

Pore refinement and chloride binding should be considered as complementary but distinct mechanisms. Pozzolanic reaction and the reaction between MK and calcite can refine the capillary pore network, thereby reducing chloride transport into the deeper matrix. Physical binding, by contrast, is associated with chloride adsorption on the surfaces of hydration products. Chemical binding involves Al-bearing Hc and Mc phases, in which chloride ions can exchange with interlayer anions and promote the formation of Friedel's salt. Together, reduced transport and enhanced physical/chemical immobilisation lower the amount of free chloride available to reach the reinforcement.

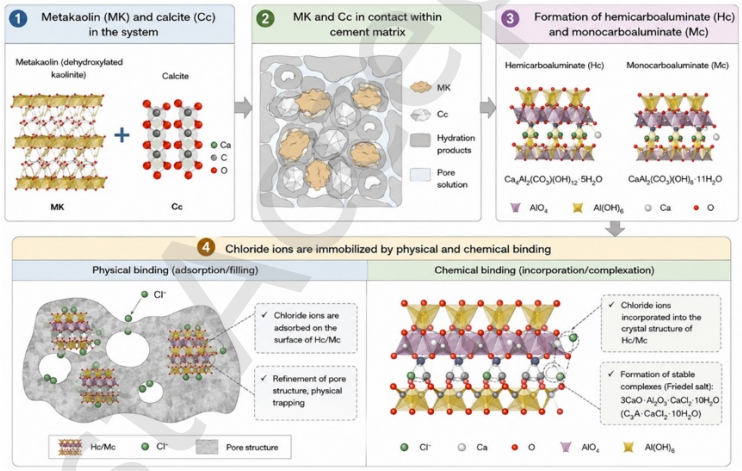


Fig. 17. Effects of MK in the chloride-binding capacity for marine structures

Laboratory experiments should be extended to long-term field exposure in submerged, tidal, splash, and marine atmospheric environments. Chloride transport and binding should be further connected with free chloride concentration, reinforcement corrosion initiation, and service-life modelling. Conventional deterministic chloride-threshold approaches may not sufficiently account for time-dependent material ageing and uncertainties in exposure and material properties [121]. Future studies could therefore integrate MK-dependent chloride transport and binding with physics-based stochastic corrosion models. Recent frameworks incorporating concrete ageing, electrochemical corrosion analysis, and machine-learning surrogate models for uncertainty quantification provide a useful methodology for such service-life assessment.

Overall, MK addition in the marine concrete structure could simultaneously reduce the chloride ingress by a denser MK-cement matrix, but also chemically adsorb chloride ions in a stable state.

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By combing these two fundamental mechanisms, MK could be considered as a favourable SCM to partially replace cement for the sustainable and low-carbon marine structures. Therefore, the microstructural effects of MK should ultimately be evaluated in terms of engineering-scale performance, particularly chloride transport to reinforcement depth, corrosion initiation time, and long-term service life under marine exposure.

6. Life-cycle sustainability of MK-based marine concrete

The end-of-life management of MK-based marine concrete should be incorporated into future sustainability assessment. Concrete recovered from decommissioned marine structures may contain residual chloride and exhibit high water absorption and complex interfacial transition zones, which can affect its reuse as recycled concrete aggregate and potentially increase subsequent corrosion risks. Future studies should integrate demolition-waste quantification, sorting, chloride assessment, recycling, and secondary utilisation with life-cycle and circular-economy evaluation [122]. The environmental benefits of MK should be evaluated using region-specific life-cycle assessment. Although MK can reduce clinker consumption, its net carbon benefit also depends on kaolin extraction and processing, calcination temperature and energy source, transportation distance, regional electricity mix, and achievable cement replacement. These factors should be assessed together with durability and service-life extension when evaluating the overall sustainability of MK-based marine concrete.

7. Conclusion and perspectives

This review was conducted to investigate the feasibility of MK-cement system to build low-carbon and durable marine structures, including on cement hydration, mechanical properties, durability, and the chloride-binding capacity. The key findings were as the follows:

- Fine particles in MK provided filler and nucleation effects, while reactive alumina reacted with portlandite to form additional C-A-S-H. In the presence of calcite, MK also promoted the formation of hemicarboaluminate (Hc) and monocarboaluminate (Mc), contributing to pore refinement and matrix densification.

- 5 wt% to 10 wt% MK addition provided favourable strength development, while the synergistic use of MK and calcite could increase the total cement replacement level to approximately 40–50 wt% while maintaining comparable compressive strength.

- MK generally reduced transport pathways by refining the pore structure. A 38.82% reduction in water absorption with 10 wt% MK was found, and together with reductions of approximately 50% in water permeability and 37% in gas permeability in other study.

- For sulphate exposure, 10 wt% MK reduced mass gain from 0.45% to 0.16%, while one reported MK system achieved a 46.1% reduction in carbonation depth. These benefits, however, strongly depended on MK dosage, fineness, reactivity, and water-to-binder ratio.

- MK improved chloride resistance through complementary physical and chemical binding mechanisms. Pore refinement and surface adsorption restricted chloride transport, while Al-rich Hc and Mc phases promoted chemical chloride immobilisation and Friedel's salt formation.

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Future research should establish clearer relationships between kaolin mineralogy, calcination conditions, MK fineness, Al/Si availability, replacement level, and pozzolanic reactivity. This is particularly important that MK performance can vary substantially with particle size and reactivity. Additionally, more studies should be conducted to investigate the formation, transformation, and long-term stability of Hc, Mc, and Friedel's salt. Future studies should determine whether physically and chemically bound chloride can be released under coupled marine deterioration conditions, particularly carbonation, sulphate exposure, wetting–drying cycles, and cracking. Overall, future development of MK-based marine concrete is expected to shift from empirical optimisation of replacement levels towards performance-based material design integrating controlled MK reactivity, chloride-binding mechanisms, long-term field exposure, probabilistic service-life prediction, and life-cycle sustainability.

Declaration of competing interest

The authors want to declare that there is not any competing interest, or personal relationships would negatively impact on the outcome of this study.

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Author contribution statement

"Author 1 is responsible for Work 1. …All the authors have approved the final manuscript." CRediT author statement (https://credit.niso.org/) is recommended to use.

Data availability

"Not applicable."

OR "The data that support the findings of this study could be downloaded from xxxxxxx / is available from the corresponding author upon reasonable request."

Use of AI statement

"None."

OR "During the preparation of this work, the author(s) used [NAME TOOL / SERVICE] in order to [REASON]. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the publication."

Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

Just Accepted

References:

[1] P. Vargas, L. Soriano, M. Borrachero, J. Tobon, J. Payá, J. Monzó, M. Tashima, Use of spent fluid catalytic cracking catalyst (fcc) in limestone calcined clay cement (lc3) systems: Studies in pastes and mortars, Journal of Cleaner Production, 451 (2024) 142177.

[2] M.F. Faraji, İ. Türkel, İ.G.M. Özkan, O.Y. Bayraktar, G. Kaplan, M. Bayram, A.C. Aydın, T. Ozbakkaloglu, Fly ash and waste brick powder-based one-part geopolymer foam concrete with enhanced thermal performance: A circular approach to construction and demolition waste utilization, Journal of Building Engineering, (2025) 114850.

[3] X. Lin, W. Li, Y. Guo, W. Dong, A. Castel, K. Wang, Biochar-cement concrete toward decarbonisation and sustainability for construction: Characteristic, performance and perspective, Journal of Cleaner Production, 419 (2023) 138219.

[4] Q. Fu, Y. Liu, D. Niu, Hydration characteristics and microstructure of limestone calcined clay cement, Journal of Building Engineering, 117 (2026) 114729.

[5] M. Dobiszewska, O. Bagcal, A. Beycioğlu, D. Goulias, F. Köksal, B. Płomiński, H. Ürünveren, Utilization of rock dust as cement replacement in cement composites: An alternative approach to sustainable mortar and concrete productions, Journal of Building Engineering, 69 (2023) 106180.

[6] X. Lin, Q.D. Nguyen, A. Castel, V.W.Y. Tam, Effect of biochar on the shrinkage deformation of ground granulated blast-furnace slag-cement mortars, Construction and Building Materials, 506 (2026) 144734.

[7] X. Lin, T. Shi, Q.D. Nguyen, A. Castel, V.W.Y. Tam, Effects of biochar on hydration, strength degradation, and alkali-silica reaction in sustainable waste glass sand-based mortars, Journal of Building Engineering, 114 (2025) 114316.

[8] A. Dixit, A. Verma, S.D. Pang, Dual waste utilization in ultra-high performance concrete using biochar and marine clay, Cement and Concrete Composites, 120 (2021) 104049.

[9] S. Gupta, H.W. Kua, C.Y. Low, Use of biochar as carbon sequestering additive in cement mortar, Cement and Concrete Composites, 87 (2018) 110-129.

[10] X. Zhao, J. Xie, Q. Dai, C. Mensah, Performance and carbon reduction of binary and ternary concrete systems with slag cement and fly ash, Journal of Building Engineering, (2026) 117087.

[11] E. Lee, S. Im, Y. Kim, K. Yang, S. Kwon, S. Jang, S. Bae, Impact of limestone on hydration kinetics and strength development of low-clinker (< 50%) high-volume slag cement pastes at different curing temperatures, Construction and Building Materials, 540 (2026) 147532.

[12] C. Klossner, H. Lyu, L. Zhu, C.S. Poon, Synthesis of carbon active eco-cement using waste glass powder and recycled concrete fine, Construction and Building Materials, 520 (2026) 146080.

[13] A. Sinha, D. Luo, S. Das, R. Mulcahy, J. Wei, Experimental and thermodynamic insights into the pozzolanic role of high-volume recycled ground waste glass in the hydration of sustainable cement binders, Sustainable Materials and Technologies, 48 (2026) e02058.

[14] Y. Ling, X. Wu, K. Tan, Z. Zou, Effect of biochar dosage and fineness on the mechanical properties and durability of concrete, Materials, 16(7) (2023) 2809.

[15] J. Tang, W. Zhou, X. Cai, D. Zhang, Feasibility of upcycling red mud for low-co2 cement via calcination: A comparative study with fa and ggbfs based in china, Journal of Cleaner Production, 476 (2024) 143734.

[16] X. Li, J. Dengler, C. Hesse, Reducing clinker factor in limestone calcined clay-slag cement using c-s-h seeding – a way towards sustainable binder, Cement and Concrete Research, 168 (2023) 107151.

Just Accepted

[17] D. Paul, K.R. Bindhu, A.M. Matos, J. Delgado, Eco-friendly concrete with waste glass powder: A sustainable and circular solution, Construction and Building Materials, 355 (2022) 129217.

[18] H. Du, K.H. Tan, Properties of high volume glass powder concrete, Cement and concrete composites, 75 (2017) 22-29.

[19] C. He, B. Osbaeck, E. Makovicky, Pozzolanic reactions of six principal clay minerals: Activation, reactivity assessments and technological effects, Cement and Concrete Research, 25(8) (1995) 1691-1702.

[20] H. Kun, T. Haoran, C. Guojun, M. Dongdong, H. Kai, L. Lulu, W. Fengyun, Research on the dynamic fracture characteristics and constitutive model of cement-metakaolin stabilized soil under freeze-thaw cycle conditions, Construction and Building Materials, 481 (2025) 141641.

[21] A.G. Alareqi, J. Gu, A.L.W. Ibrahim, E.E. Nyakilla, A. Salah, G. Al-khulaidi, Enhancing the durability of oil and gas wells using metakaolin-modified cement: An investigation of compressive and shear bond strengths at 95 and 180 °c, Construction and Building Materials, 458 (2025) 139572.

[22] R. Oscar, Metallurgical characterization of kaolin from atacama, chile. Rem, int, Eng. Journal, 69(4) (2016).

[23] A.A. Raheem, R. Abdulwahab, M.A. Kareem, Incorporation of metakaolin and nanosilica in blended cement mortar and concrete- a review, Journal of Cleaner Production, 290 (2021) 125852.

[24] R. Fernandez, F. Martirena, K.L. Scrivener, The origin of the pozzolanic activity of calcined clay minerals: A comparison between kaolinite, illite and montmorillonite, Cement and Concrete Research, 41(1) (2011) 113-122.

[25] Q. Huang, Q. Wang, Z. Zhang, C. Shen, W. Zhou, X. Xu, X. Zhu, Effect of metakaolin fineness on performance and microstructure of cement-based materials, Journal of Building Engineering, 99 (2025) 111577.

[26] C. Liang, Y. Xing, X. Hou, Multi-scale study on mechanical performance optimization mechanisms of aeolian sand cement-based materials incorporating discarded mask fibres and metakaolin, Construction and Building Materials, 470 (2025) 140653.

[27] H. El-Diadamony, A.A. Amer, T.M. Sokkary, S. El-Hoseny, Hydration and characteristics of metakaolin pozzolanic cement pastes, HBRC Journal, 14(2) (2018) 150-158.

[28] N. Kumar, A study of metakaolin and silica fume used in various cement concrete designs, International Journal of Enhanced Research in Science Technology & Engineering, 3(6) (2014) 176-181.

[29] O. Keleştemur, B. Demirel, Effect of metakaolin on the corrosion resistance of structural lightweight concrete, Construction and Building Materials, 81 (2015) 172-178.

[30] L. Campagiorni, M. Tonelli, F. Ridi, Synergistic effect of limestone and supplementary cementitious materials in ternary blended cements, Current Opinion in Colloid & Interface Science, 75 (2025) 101885.

[31] Q. Qin, Q. Meng, M. Gan, J. Zhang, P. Yi, Synergistic effects of waste coral powder and metakaolin in cement pastes: Hydration, pore structure, rheology, and strength, Journal of Building Engineering, 97 (2024) 111001.

[32] M. Antoni, J. Rossen, F. Martirena, K. Scrivener, Cement substitution by a combination of metakaolin and limestone, Cement and concrete research, 42(12) (2012) 1579-1589.

[33] Z. Zhang, H. Wang, X. Yao, Y. Zhu, Effects of halloysite in kaolin on the formation and properties of geopolymers, Cement and Concrete Composites, 34(5) (2012) 709-715.

[34] L. Trusilewicz, F. Fernández-Martínez, V. Rahhal, R. Talero, Tem and saed characterization of metakaolin. Pozzolanic activity, Journal of the American Ceramic Society, 95(9) (2012) 2989-2996.

Just Accepted

[35] J. TORRES AGREDO, R. MEJÍA DE GUTIÉRREZ, Influence of the mineralogical composition of kaolins on the performance of added mortars with mk, Dyna, 74(153) (2007) 61-67.

[36] L. Li, J. Xie, B. Zhang, Y. Feng, J. Yang, A state-of-the-art review on the setting behaviours of ground granulated blast furnace slag- and metakaolin-based alkali-activated materials, Construction and Building Materials, 368 (2023) 130389.

[37] D.K. Panesar, R. Zhang, Performance comparison of cement replacing materials in concrete: Limestone fillers and supplementary cementing materials – a review, Construction and Building Materials, 251 (2020) 118866.

[38] K. Weise, N. Ukrainczyk, E. Koenders, Pozzolanic reactions of metakaolin with calcium hydroxide: Review on hydrate phase formations and effect of alkali hydroxides, carbonates and sulfates, Materials & Design, 231 (2023) 112062.

[39] W. Zhao, Y. Chen, Z. Liu, L. Wang, X. Li, Effects of surface-modified coal-bearing metakaolin and graphene oxide on the properties of cement mortar, Construction and Building Materials, 372 (2023) 130796.

[40] D. Ndahirwa, H. Zmamou, H. Lenormand, N. Leblanc, The role of supplementary cementitious materials in hydration, durability and shrinkage of cement-based materials, their environmental and economic benefits: A review, Cleaner Materials, 5 (2022) 100123.

[41] Y. Asghari, S. Esmaeil Mohammadyan-Yasouj, S. Saeid Rahimian Koloor, Utilization of metakaolin on the properties of self-consolidating concrete: A review, Construction and Building Materials, 389 (2023) 131605.

[42] M.F. Ghazy, E.S.A. Maaty, M.A. Elaty, A.a.A. Alrwashdeh, A comprehensive review of limestone calcined clay cement (lc3): Environmental and properties benefits, challenges, opportunities, and future directions, Results in Engineering, 28 (2025) 108319.

[43] S.A. Mana, M. Hanafiah, A. Chowdhury, Environmental characteristics of clay and clay-based minerals. Geol ecol landsc 1 (3): 155–161, 2017.

[44] B.B. Lázaro, Halloysite and kaolinite: Two clay minerals with geological and technological importance, Revista de la Academia de Ciencias Exactas, Físicas, Químicas y Naturales de Zaragoza, 70 (2015) 7-38.

[45] K. Al-Jabri, H. Shoukry, Influence of nano metakaolin on thermo-physical, mechanical and microstructural properties of high-volume ferrochrome slag mortar, Construction and Building Materials, 177 (2018) 210-221.

[46] G.F. Huseien, J. Mirza, M. Ismail, S. Ghoshal, M.A.M. Ariffin, Effect of metakaolin replaced granulated blast furnace slag on fresh and early strength properties of geopolymer mortar, Ain Shams Engineering Journal, 9(4) (2018) 1557-1566.

[47] K. Boakye, M. Khorami, M. Saidani, E. Ganjian, A. Dunster, M. Tyrer, A. Ehsani, Influence of calcining temperature on the mineralogical and mechanical performance of calcined impure kaolinitic clays in portland cement mortars, Journal of Materials in Civil Engineering, 36(4) (2024) 04024040.

[48] G.M. Ayininuola, O.A. Adekitan, Characterization of ajebo kaolinite clay for production of natural pozzolan, International Journal of Civil, Environmental, Structural, Construction and Architectural Engineering, 10(9) (2016) 1212-1219.

[49] K. Abdelli, M. Tahlaiti, R. Belarbi, M.N. Oudjit, Influence of the pozzolanic reactivity of the blast furnace slag (bfs) and metakaolin on mortars, Energy Procedia, 139 (2017) 224-229.

[50] D. Adesanya, A. Raheem, Development of corn cob ash blended cement, Construction and Building Materials, 23(1) (2009) 347-352.

[51] S. Overmann, A. Vollpracht, T. Matschei, Reactivity of calcined clays as scm—a review, Materials, 17(2) (2024) 312.

Just Accepted

[52] N. Garg, J. Skibsted, Dissolution kinetics of calcined kaolinite and montmorillonite in alkaline conditions: Evidence for reactive al (v) sites, Journal of the American Ceramic Society, 102(12) (2019) 7720-7734.

[53] M. Stefanidou, E.-C. Tsardaka, E. Pavlidou, Influence of nano-silica and nano-alumina in lime-pozzolan and lime-metakaolin binders, Materials Today: Proceedings, 4(7) (2017) 6908-6922.

[54] O.R. Alonge, M.B. Ramli, T.J. Lawalson, Properties of hybrid cementitious composite with metakaolin, nanosilica and epoxy, Construction and Building Materials, 155 (2017) 740-750.

[55] B. Akcay, M.A. Tasdemir, Performance evaluation of silica fume and metakaolin with identical finenesses in self compacting and fiber reinforced concretes, Construction and Building Materials, 185 (2018) 436-444.

[56] S.H. Chu, A.K.H. Kwan, Co-addition of metakaolin and silica fume in mortar: Effects and advantages, Construction and Building Materials, 197 (2019) 716-724.

[57] P. Zhan, X. Sun, D. Wang, D. Wang, W. Lin, X. Lin, J. Wang, V.W.Y. Tam, Synergistic effects of metakaolin and limestone on early hydration kinetics, strength development, and microstructure of low water-to-binder ratio cement composites, Case Studies in Construction Materials, 24 (2026) e06210.

[58] T. Sundararajan, Comparative study of initial and final setting times of lc3 and opc concrete mixes, Materials Research Innovations, 29(1) (2021) 14-20.

[59] B.H. Zaribaf, K.E. Kurtis, Admixture compatibility in metakaolin–portland-limestone cement blends, Materials and Structures, 51(1) (2018) 33.

[60] Y. Li, Impact of limestone and calcined clay proportions on setting times of lc3 cement, Cement and Concrete Research, 157 (2023) 106974.

[61] M. Sharma, S. Bishnoi, F. Martirena, K. Scrivener, Limestone calcined clay cement and concrete: A state-of-the-art review, Cement and Concrete Research, 149 (2021) 106564.

[62] F. Zunino, K. Scrivener, The reaction between metakaolin and limestone and its effect in porosity refinement and mechanical properties, Cement and Concrete Research, 140 (2021) 106307.

[63] F.A. Zunino Sommariva, Limestone calcined clay cements (lc3): Raw material processing, sulfate balance and hydration kinetics, EPFL, 2020.

[64] J. Ambroise, S. Maximilien, J. Pera, Properties of metakaolin blended cements, Advanced Cement Based Materials, 1(4) (1994) 161-168.

[65] L. Wang, H. Yang, S. Zhou, E. Chen, S.W. Tang, Mechanical properties, long-term hydration heat, shinkage behavior and crack resistance of dam concrete designed with low heat portland (lhp) cement and fly ash, Construction and Building materials, 187 (2018) 1073-1091.

[66] Y. Yu, C. Gunasekara, Y. Elakneswaran, D. Robert, D.W. Law, S. Setunge, On the hydration of limestone calcined kaolinitic clay cement and energy-efficient production, Cement and Concrete Composites, 153 (2024) 105698.

[67] J. Chen, P.L. Ng, S. Chu, G. Guan, A. Kwan, Ternary blending with metakaolin and silica fume to improve packing density and performance of binder paste, Construction and Building Materials, 252 (2020) 119031.

[68] R. San Nicolas, M. Cyr, G. Escadeillas, Characteristics and applications of flash metakaolins, Applied Clay Science, 83 (2013) 253-262.

[69] R. San Nicolas, M. Cyr, G. Escadeillas, Performance-based approach to durability of concrete containing flash-calcined metakaolin as cement replacement, Construction and Building Materials, 55 (2014) 313-322.

Just Accepted

[70] J. Ahmad, K.J. Kontoleon, A. Majdi, M.T. Naqash, A.F. Deifalla, N. Ben Kahla, H.F. Isleem, S.M. Qaidi, A comprehensive review on the ground granulated blast furnace slag (ggbs) in concrete production, Sustainability, 14(14) (2022) 8783.

[71] M.J. Geu, Y. Zhuge, X. Ma, T.M. Pham, Optimising calcination temperature for high reactivity metakaolin: Influence on amorphous content, mineralogy and microstructure, Construction and Building Materials, 489 (2025) 142431.

[72] D.L. Pillay, O.B. Olalusi, M.W. Kiliswa, P.O. Awoyera, J.T. Kolawole, A.J. Babafemi, Engineering performance of metakaolin based concrete, Cleaner Engineering and Technology, 6 (2022) 100383.

[73] H.M. Khater, Influence of metakaolin on resistivity of cement mortar to magnesium chloride solution, Ceramics-Silikáty, 54(4) (2010) 325-333.

[74] A. Belaid, S. Khaled, H. Brahim, K. Salim, S. Brahim, N. Mesrati, Effect of metakaolin as partially cement replacement on the compressive strength of standard mortars, Revista Romana de Inginerie Civila, 12(2) (2021) 268-280.

[75] P. Dinakar, P.K. Sahoo, G. Sriram, Effect of metakaolin content on the properties of high strength concrete, International Journal of Concrete Structures and Materials, 7(3) (2013) 215-223.

[76] A. Abbasi Dezfouli, Experimental investigation into the metakaolin used in concrete, Journal of Civil Engineering and Materials Application, 5(2) (2021) 67-80.

[77] M. Atasever, S.T. Erdoğan, Effects of clay type and component fineness on the hydration and properties of limestone calcined clay cement, Materials and Structures, 57(8) (2024) 183.

[78] A. Alujas Diaz, R.S. Almenares Reyes, T. Hanein, E.F. Irassar, M. Juenger, F. Kanavaris, M. Maier, A.T. Marsh, T. Sui, K.-C. Thienel, L. Valentini, B. Wang, F. Zunino, R. Snellings, Properties and occurrence of clay resources for use as supplementary cementitious materials: A paper of rilem tc 282-ccl, Materials and Structures, 55(5) (2022) 139.

[79] Y. Dhandapani, M. Santhanam, Investigation on the microstructure-related characteristics to elucidate performance of composite cement with limestone-calcined clay combination, Cement and Concrete Research, 129 (2020) 105959.

[80] H. Du, S. Dai Pang, Value-added utilization of marine clay as cement replacement for sustainable concrete production, Journal of Cleaner Production, 198 (2018) 867-873.

[81] Q.D. Nguyen, S. Afroz, A. Castel, Influence of calcined clay reactivity on the mechanical properties and chloride diffusion resistance of limestone calcined clay cement (lc3) concrete, Journal of Marine Science and Engineering, 8(5) (2020) 301.

[82] Y. Bu, J. Du, S. Guo, H. Liu, C. Huang, Properties of oil well cement with high dosage of metakaolin, Construction and Building Materials, 112 (2016) 39-48.

[83] A. Saand, K. Ali, A. Kumar, N. Bheel, M.A. Keerio, Effect of metakaolin developed from natural material soorh on fresh and hardened properties of self-compacting concrete, Innovative Infrastructure Solutions, 6(3) (2021) 166.

[84] T. Singh, R. Siddique, S. Sharma, Effectiveness of using metakaolin and fly ash as supplementary cementitious materials in pervious concrete, European journal of environmental and civil engineering, 26(15) (2022) 7359-7382.

[85] J. Salimi, A.M. Ramezanianpour, M.J. Moradi, Studying the effect of low reactivity metakaolin on free and restrained shrinkage of high performance concrete, Journal of Building Engineering, 28 (2020) 101053.

[86] R. Muduli, B.B. Mukharjee, Effect of incorporation of metakaolin and recycled coarse aggregate on properties of concrete, Journal of Cleaner Production, 209 (2019) 398-414.

Just Accepted

[87] H.-S. Kim, S.-H. Lee, H.-Y. Moon, Strength properties and durability aspects of high strength concrete using korean metakaolin, Construction and building materials, 21(6) (2007) 1229-1237.

[88] N. Singh, S. Singh, Carbonation and electrical resistance of self compacting concrete made with recycled concrete aggregates and metakaolin, Construction and Building Materials, 121 (2016) 400-409.

[89] W. Li, L. Hua, Y. Shi, P. Wang, Z. Liu, D. Cui, X. Sun, Influence of metakaolin on the hydration and microstructure evolution of cement paste during the early stage, Applied Clay Science, 229 (2022) 106674.

[90] G. Medjigbodo, E. Rozière, K. Charrier, L. Izoret, A. Loukili, Hydration, shrinkage, and durability of ternary binders containing portland cement, limestone filler and metakaolin, Construction and Building Materials, 183 (2018) 114-126.

[91] Y. Luo, X. Gao, D. Wang, Y. Liu, Q. Zhang, J. Li, Z. Tian, G. Xue, Study on the efflorescence behavior of concrete by adding metakaolin, Journal of Building Engineering, 83 (2024) 108396.

[92] H. Maraghechi, F. Avet, H. Wong, H. Kamyab, K. Scrivener, Performance of limestone calcined clay cement (lc3) with various kaolinite contents with respect to chloride transport, Materials and structures, 51(5) (2018) 125.

[93] Z. Shi, M.R. Geiker, B. Lothenbach, K. De Weerdt, S.F. Garzón, K. Enemark-Rasmussen, J. Skibsted, Friedel's salt profiles from thermogravimetric analysis and thermodynamic modelling of portland cement-based mortars exposed to sodium chloride solution, Cement and Concrete Composites, 78 (2017) 73-83.

[94] M. Nas, S. Kurbetci, Durability properties of concrete containing metakaolin, Advances in concrete construction, 6(2) (2018) 159.

[95] M. Bansal, M. Bansal, A. Bahrami, B. Krishan, R. Garg, Y.O. Özkılıç, E. Althaqafi, Retracted: Influence of pozzolanic addition on strength and microstructure of metakaolin-based concrete, Plos one, 19(4) (2024) e0298761.

[96] A. Joshaghani, M.A. Moeini, M. Balapour, Evaluation of incorporating metakaolin to evaluate durability and mechanical properties of concrete, Advances in concrete construction, 5(3) (2017) 241.

[97] M.A. Keerio, A. Saand, R. Chaudhry, N. Bheel, N. ul Karim Bhatti, S. Soohu, The effect of local metakaolin developed from natural material soorh on selected properties of concrete/mortar, Silicon, 14(4) (2022) 1807-1816.

[98] M. Shekarchi, A. Bonakdar, M. Bakhshi, A. Mirdamadi, B. Mobasher, Transport properties in metakaolin blended concrete, Construction and Building Materials, 24(11) (2010) 2217-2223.

[99] Z. Shi, S. Ferreiro, B. Lothenbach, M.R. Geiker, W. Kunther, J. Kaufmann, D. Herfort, J. Skibsted, Sulfate resistance of calcined clay–limestone–portland cements, Cement and Concrete Research, 116 (2019) 238-251.

[100] A. Favier, K. Scrivener, Alkali silica reaction and sulfate attack: Expansion of limestone calcined clay cement, Calcined Clays for Sustainable Concrete: Proceedings of the 2nd International Conference on Calcined Clays for Sustainable Concrete, Springer, 2017, pp. 165-169.

[101] T. Boubekeur, B. Boulekbache, K. Aoudjane, K. Ezziane, E.-H. Kadri, Prediction of the durability performance of ternary cement containing limestone powder and ground granulated blast furnace slag, Construction and Building Materials, 209 (2019) 215-221.

[102] R. Sharma, R.A. Khan, Influence of copper slag and metakaolin on the durability of self compacting concrete, Journal of Cleaner Production, 171 (2018) 1171-1186.

[103] W. Song, T. Guo, P. Han, X. Wang, F. Ma, B. He, Durability study and mechanism analysis of red mud-coal metakaolin geopolymer concrete under a sulfate environment, Construction and Building Materials, 409 (2023) 133990.

Just Accepted

[104] M. Beulah, M. Prahallada, Effect of replacement of cement by metakalion on the properties of high performance concrete subjected to hydrochloric acid attack, International Journal of Engineering Research and Applications, 2(6) (2012) 033-038.

[105] D. Viswanadha Varma, G. Rama Rao, P. Markandeya Raju, M. Pavan Kumar, Compressive strength and durability of metakaolin blended concrete exposed to acid and sulphate attack, IOP Conference Series: Materials Science and Engineering, IOP Publishing, 2021, p. 012004.

[106] R. Ian Gilbert, A. Castel, I. Khan, W. South, J. Mohammadi, An experimental study of autogenous and drying shrinkage, High Tech Concrete: Where Technology and Engineering Meet: Proceedings of the 2017 fib Symposium, held in Maastricht, The Netherlands, June 12-14, 2017, Springer, 2017, pp. 33-41.

[107] A. ElSafty, A. Abdel-Mohti, Investigation of likelihood of cracking in reinforced concrete bridge decks, International Journal of Concrete Structures and Materials, 7(1) (2013) 79-93.

[108] Q.T. Phung, N. Maes, D. Jacques, G. De Schutter, G. Ye, J. Perko, Modelling the carbonation of cement pastes under a co2 pressure gradient considering both diffusive and convective transport, Construction and Building Materials, 114 (2016) 333-351.

[109] L. Li, M.H. Hubler, Y. Xi, Theoretical modeling on chemical composition and mechanical properties of well cement under carbonation reactions, Journal of Cleaner Production, 276 (2020) 124270.

[110] T. Ayub, S.U. Khan, F.A. Memon, Mechanical characteristics of hardened concrete with different mineral admixtures: A review, The Scientific World Journal, 2014(1) (2014) 875082.

[111] D.K. Ashish, Concrete made with waste marble powder and supplementary cementitious material for sustainable development, Journal of Cleaner Production, 211 (2019) 716-729.

[112] R. Bucher, P. Diederich, G. Escadeillas, M. Cyr, Service life of metakaolin-based concrete exposed to carbonation: Comparison with blended cement containing fly ash, blast furnace slag and limestone filler, Cement and Concrete Research, 99 (2017) 18-29.

[113] S. Barbhuiya, P. Chow, S. Memon, Microstructure, hydration and nanomechanical properties of concrete containing metakaolin, Construction and Building Materials, 95 (2015) 696-702.

[114] Y. Patrisia, D.W. Law, J. Zhang, Quantifying concrete recarbonation potential: A life cycle approach to carbon uptake, Environmental Impact Assessment Review, 118 (2026) 108300.

[115] Y. Bu, R. Ma, J. Du, S. Guo, H. Liu, L. Zhao, Utilization of metakaolin-based geopolymer as a mud-cake solidification agent to enhance the bonding strength of oil well cement–formation interface, Royal Society Open Science, 7(2) (2020).

[116] J. Zuquan, Z. Xia, Z. Tiejun, L. Jianqing, Chloride ions transportation behavior and binding capacity of concrete exposed to different marine corrosion zones, Construction and Building Materials, 177 (2018) 170-183.

[117] J. Wang, Q. Wang, Y. Zhao, P. Li, T. Ji, G. Zou, Y. Qiao, Z. Zhou, G. Wang, D. Song, Research progress of macrocell corrosion of steel rebar in concrete, Coatings, 13(5) (2023) 853.

[118] G. Dhinakaran, S. Thilgavathi, J. Venkataramana, Compressive strength and chloride resistance of metakaolin concrete, KSCE Journal of Civil Engineering, 16(7) (2012) 1209-1217.

[119] A. Babaahmadi, A. Machner, W. Kunther, J. Figueira, P. Hemstad, K. De Weerdt, Chloride binding in portland composite cements containing metakaolin and silica fume, Cement and Concrete Research, 161 (2022) 106924.

[120] A. Ipavec, R. Gabrovšek, T. Vuk, V. Kaučič, J. Maček, A. Meden, Carboaluminate phases formation during the hydration of calcite-containing portland cement, Journal of the American Ceramic Society, 94(4) (2011) 1238-1242.

Just Accepted

[121] Y. Yu, B. Dong, W. Gao, A. Sofi, Physics-based stochastic aging corrosion analysis assisted by machine learning, Probabilistic Engineering Mechanics, 69 (2022) 103270.

[122] W. Sun, Q. Tushar, G. Zhang, A. Song, L. Hou, J. Zhang, S. Wang, An analytical review of construction and demolition waste management and quantification methods using a science mapping approach, Recycling, 10(3) (2025) 115.

Just Accepted