# Chapter 2
# Literature Review

## 2.1 Metakaolin

Metakaolin is a highly reactive pozzolanic material obtained through kaolin clay's calcination at temperatures ranging from 700 to 850 ºC [44,45]. The resulting material is composed of approximately 50-55% $SiO_2$ and 40-45% $Al_2O_3$ and has been shown to increase compressive strength in high-performance concretes and mortars at early ages [46]. During calcination, kaolinite loses OH lattice water and transforms into metakaolinite, a highly reactive material with low structural order. This makes it an excellent pozzolan for use in cement-based composites, where it reacts well with lime and forms hydrated Ca and Al silicate compounds [47].

Unlike other pozzolans, which are by-products or secondary products, MK is a primary product with properties, and its uses are as a pozzolanic micro-filler similar to silica fume [48]. The addition of Metakaolin has been reported to yield higher strengths and a faster rate of strength gain, increasing the elastic modulus of concrete [49]. The use of Metakaolin also leads to refinement in the microstructure of the cement paste, with a greater amount of secondary CSH being produced by the pozzolanic reaction of Metakaolin, leading to a greater number of very small pores [49,50] and thus enhances durability. One of the major benefits of using Metakaolin in mortar and concrete is the removal of CH, which is produced during cement hydration and is associated with poor durability. CH removal significantly influences resistance to sulphate attack and alkali-silica reaction (ASR). Also, it provides enhanced strength derived from the additional cementitious phases generated by the reaction of CH with MK [51].

Metakaolin offers several benefits in the construction sector, such as heightened compressive and flexural strengths, decreased permeability, improved resistance to chemical attacks, enhanced durability, minimised effects of ASR, reduced shrinkage, and improved workability for concrete [52]. These advantages make it valuable for producing high-performance, high-strength, lightweight, and precast concrete with improved finishability, colour, and appearance.

### 2.1.1 Pozzolanic reaction mechanism

Thermal activation of kaolinite-rich soils between 600-900º C through dihydroxylation results in the breakdown of the material, causing a change in the silica and alumina layers and producing Metakaolin with high reactivity ($Al_2O_3.2SiO_2$) or $AS_2$ [53,54]. The main reaction occurs between $AS_2$ and CH, which originates from cement hydration in the presence of water, leading to the formation of secondary hydrates such as calcium silica hydrate (C-S-H), as well as crystalline products such as calcium aluminate hydrates and alumino-silicate hydrates ($C_4AH_{13}$, $C_3AH_6$, and $C_2ASH_8$, also known as stratlingite) [45,55,56]. The formation of crystalline products depends on the $AS_2$ to CH ratio and the reaction temperature [57–59]

Metakaolin's reaction rate is influenced by several factors, such as the temperature at calcination, processing conditions, and the clay type and its purity. Additionally, the degree of reactivity in Metakaolin is associated with the level of penta-coordinated aluminum ions, which are created during the dehydroxylation procedure [30,60,61]. Thus, the ideal replacement levels of Portland cement with Metakaolin are determined by changes in the type and level of reaction products, which are influenced by factors such as composition, temperature, and reaction time within the OPC-MK system.

To avoid weakening the clay, it is essential to purify it using standard mineral processing methods. The activation temperature, which varies depending on the mineral type, is crucial and typically ranges between 700 and 800°C. Concrete that includes clay with 90% kaolin has shown increased compressive strength due to lower CH content.

The Chapelle test can measure the pozzolanic reactivity. TG and DTA can measure CH in cured concrete, while chemical determination can detect unreacted pozzolan in hydrated PC-pozzolan pastes to assess pozzolanic reactivity. To evaluate the pozzolanic activity of MK, the heat evolution of MK-PC mortars can be compared to SF-PC and FA-PC mortars [62–65]. The hydration products largely depend on the composition of the cement. Therefore, the pozzolanic activity with the CH also depends on the cement composition, water-to-binder ratio (W/B) and, of course, the purity of the Metakaolin, as discussed above.

The pozzolanic reactivity of MK is affected by the temperature at which the clay is calcined. When clay is heated at a temperature of 500 to 900°C and loses its hydroxyls, its structure becomes disordered and collapses, and at this point, the clay becomes highly reactive.[66]. Kaolinites are usually heated in rotary kilns or fluidised bed processes, which take hours to calcine. However, flash-calcination is a quicker method that heats and cools the clay rapidly in seconds. Salvador and Davies used this method and discovered that the quality of the MK depends on the temperature (500-1000°C) and time (0.5 to 12 seconds) of flash-calcination. This method is more effective than soaking for producing highly active MK [67].

### 2.1.2 Effect of MK on the fresh properties of mortar/concrete

Wild et al.[68] found that increasing the level of MK replacement increased the slump value and SP demand of concrete, while Brooks and Johari [69] reported a reduction in slump values and an increase in setting times with MK inclusion. Li and Ding [70] found that fluidity became poorer with the inclusion of MK into cement. Badogiannis et al. [71] reported that the blended cement demanded more water and that setting times were affected by MK content, with 10% MK content exhibiting similar setting times as of reference and 20% MK content exhibiting delayed setting times.

Zhang et al. [72] reported that adding ultrafine Metakaolin and a certain amount of polycarboxylate superplasticiser to concrete effectively improved workability. Dinakar et al. [73] found that replacing cement with MK resulted in a slight decrease in the plastic density of concrete due to the lower specific gravity of MK. Additionally, the slump value decreased, and the super plasticiser demand increased significantly as the MK content increased from 0 to 15%. Cassagnabère et al. [74] observed a decrease in a slump and an increase in viscosity values when the roundness of MK particles decreased and ruggedness increased. On the other hand, flash calcination smoothed the surface of the smallest MK particles, thereby maintaining flow properties similar to reference mortar, even at a 12.5% MK replacement level.

Chu and Kwan's study [75] indicates that adding 20% MK to mortar samples with different water-to-binder ratios can marginally improve workability, flow diameter, and flow rate by enhancing dense packing and filling. However, Chen et al. [76] observed that the workability of mortar primarily depends on W/B and not the amount of MK used, and adding MK can lead to a slight reduction in workability.

MK can enhance cohesiveness and reduce concrete consistency, making it more pumpable and easy to place without bleeding [76,77]. This makes it an appropriate substitute for self-compacting concrete (SCC), even though there might be a slight adverse effect on the SCC slump [78]. Meddah et al. [79] found that specimens containing MK required 2-4% less water than SF. This is because both MK and SF have high surface areas, improving concrete's normal consistency. Other researchers [77,80] have also reported that MK-containing specimens require less water-reducing admixture than SF-containing specimens.

Factors such as cement type, fineness, replacement level and reactivity of MK, Al2O3 content, and superplasticiser (SP) dosage influence the initial and final setting time of concrete and mortar containing MK. Meddah et al. [79] observed that MK can accelerate setting time more than SF due to its high reactivity and pozzolanic activity in early ages, while Wild and Khatib [81] reported retarding effect caused by slower hydration kinetics than Portland cement, C3A dilution, and reduced clinker-free lime. Brooks et al. [82]and Batis et al. [83] found that replacing some cement with MK prolonged setting time, although some studies showed moderate effects or decreases in setting time after MK addition [84–86].

Jiang et al. [87] reported that mortars with 0%, 6%, 10%, and 14% MK had the highest levels of heat flow. Moreover, using 10% or 14% MK in mortars delayed the starting acceleration period and decreased the peak of hydration heat. Other studies have shown that mixes with MK produced almost the same heat as OPC or slightly more in the early stages due to accelerated cement hydration and a high aluminum composition [65,88-91].

### 2.1.3 Effect of MK on mechanical properties of mortar/concrete

#### *i* ***Compressive strength***

According to Wild et al. [30] incorporating MK into concrete as a partial replacement for cement improved its compressive strength, with the maximum strength achieved at a 20% replacement level. They identified three factors that influenced the strength development in MK concrete: the filler effect of MK, which had an immediate impact, the acceleration of cement hydration within the first 24 hours, and the pozzolanic reaction, which had its maximum effect within 14 days. Compared to the reference concrete, the study noticed the strength development in MK concrete for up to 90 days. Similar findings were reported in the study by Curcio et al. [32] who found mortars with 15% MK had a higher gain in strength even after 180 days.

Brooks and Johari [69] reported an increase in compressive strength as the MK replacement level increased up to 15%, but the maximum strength was observed at a 10% replacement level, which was similar to the results obtained by Li and Ding [70]. Poon et al. [92] found that cement paste with 10% MK had the highest strength among samples with MK content varying from 5% to 20%. All samples with MK outperformed the control at all ages up to 90 days. According to Jin and Li [93], compared to silica fume, slag, and fly ash, MK exhibited the best performance in enhancing the strength of young concrete with an age of less than seven days.

Badogiannis et al. [94] investigated the effects of incorporating MK (MKG) derived from poor Greek kaolin and commercially available pure Metakaolin (MKC) as replacements for cement and sand at levels of 10% and 20% on the compressive strength of concrete. The results showed that replacement with MKG resulted in higher strength at 10% cement replacement and 20% sand replacement, while for MKC, the higher strength was observed at 20% cement replacement and 10% sand replacement. In all cases, the concrete with MK exhibited higher strength than the control concrete up to 90 days, except for the three days when the control concrete gave the higher strength. Similarly, Badogiannis et al. [71] investigated the effect of incorporating five types of MK derived from poor Greek kaolins with varying metakaolinite content on the compressive strength of cement paste for up to 180 days. It was found that MK significantly improved the strength of cement paste from day 2, particularly at 28 and 180 days, with 10% MK being the optimal level for strength enhancement.

Furthermore, Potgieter-Vermaak and Potgieter [95] studied the effect of incorporating 10-30% MK, activated at temperatures ranging from 550–850 °C for 30–60 minutes, on the compressive strength of mortar for 28 days. The results indicated that the optimal activation temperature for Metakaolin from kaolin was 700 °C, preferably up to 750 °C, and that the compressive strength of mortar increased with curing time and was highly influenced by activation temperature. However, metakaolin concentration did not significantly affect mortar strength, and the mortars with MK activated for 60 minutes had slightly higher compressive strength.

The density of concrete can be improved by the formation of CSH, CAH, and CSAH through the pozzolanic reaction of MK, resulting in the refinement of the pore structure, particularly at the ITZ [96]. Nežerka et al. [97] found that replacing cement with 10% to 20% MK reduced the thickness of the ITZ in concrete by 48% and 15%, respectively. However, a negative effect on ITZ and strength was observed at the 30% MK replacement level. The porosity at the ITZ region is 30% higher than within the cement matrix, according to Scrivener et al. [98]; thus, ITZ densification enhances compressive strength. Furthermore, replacing MK up to 25% could increase compressive strength, as observed in other studies [31,97,99,100].

However, replacing cement with high levels of MK can harm concrete's mechanical properties for various reasons. Insufficient CH needed for pozzolanic activity, dilution effect (high water to cement ratio) in high replacement levels, deceleration of hydration by increasing aluminium ions, retardation of CSH nucleation, and C3S hydration are some of the reasons [101–106]. As a result, in most studies, a 10% to 20% MK replacement was reported as the optimum level for improving compressive strength.

MK-incorporated concrete has a high-early strength development, making it suitable for use in prestressed concrete where early strength is crucial [31,107–109]. The impact of MK on the strength properties of concrete is influenced by various factors such as W/B, the reactivity and composition of MK, the fineness of MK particles, concrete age, and the specific mixing procedures employed [77]. Sullivan et al. [110] observed that irregularities in the test results of a particular type of MK could be attributed to the high fineness of MK and agglomeration during the concrete mixing process, highlighting the importance of proper mixing.

Perlot et al. [111] reported that the slurry form of MK had better dispersion and reactivity than the powdered form and suggested thorough mixing of dry materials, including MK, for several minutes before adding water to improve particle dispersion. Ilic et al. [112] investigated the effects of autoclave curing on mortars containing 10%, 20%, and 30% MK and found that autoclave curing resulted in 20-30% lower 28-day compressive strength than traditional curing.

### *ii* ***Tensile strength, flexural strength and modulus of elasticity***

Adding MK to concrete enhanced its tensile strength, flexural strength, and MOE up to a certain level of their replacement [99,113–116]. According to Qian and Li [114] the tensile strength increased as MK content increased to 15%. However, the bending strength had a negligible effect at 5% MK replacement but increased by 32% and 38% at 10% and 15% replacements, respectively, after 28 days. However, according to Courard et al. [117] the bending strength of MK with a 5-20% replacement level had almost the same strength as the control sample at 28 days.

According to various studies, the effect of MK on the splitting tensile strength is relatively low [77]. Guneyisi et al. [118] observed that incorporating MK up to 20% positively affected tensile strength, which aligns with the findings of Khatib et al. [119], who reported enhanced strength and dynamic modulus when using up to 20% MK. However, Sullivan et al. [110] found that MK resulted in a decrease in dynamic Young's modulus. Furthermore, it was reported that the modulus of elasticity (MOE) is primarily influenced by the aggregate phase [114,120–123], and the effect of MK on MOE was minimal compared to its effect on compressive strength [77]. Al-alaily and Hassan [124] reported that the W/B, percentage of MK, and binder content were the primary controlling parameters for MOE. Barbhuiya et al. [125] conducted a statistical nano-indentation analysis, which indicated that incorporating MK did not alter the hardness or modulus of the CSH gel.

### 2.1.4 Effect of MK on durability properties of mortar/concrete

#### *i* ***Water absorption***

The connection of the capillary pores, the distribution of pore sizes, and the ITZ thickness are the primary determinants of water absorption, porosity, and sorptivity [126,127]. Numerous studies indicated that incorporating MK into concrete lowers water absorption and sorptivity by decreasing the number of connected capillary pores, improving pore size distribution, and reducing ITZ thickness [65,125,126,128–130]. However, few studies also reported the adverse effect of MK as the water absorption increased with the use of MK. Courard et al. [117] found that elevating the MK content in concrete mixtures resulted in a rise in water absorption after 28 days and 14 months. Khatib and Clay [123] observed that increasing the MK content of concrete mixtures led to increased water absorption at all curing times. Razak and others corroborated these findings in the same year.

#### *ii* ***Aggressive environment***

The study conducted by Marwan et al. [131] found that incorporating laterite soil calcined at 800°C as an admixture in concrete, up to 50% replacement level, improved the concrete's resistance to the harmful effects of seawater and acidic solutions. Additionally, concrete with 30% MK replacement eliminated CH from the cement hydration process, resulting in the best overall performance of the concrete. The durability of mortars blended with MK in seawater was studied by Bosc et al. [132]. According to their findings, the mortars that included MK and a melamine superplasticiser exhibited superior performance to the control mortars. These mortars showed a 40% increase in strength and a 60% reduction in dimensional change. The specimens were cured in air at 98% relative humidity for 28 days and then exposed to seawater at 20°C and 30°C.

In their study, Cabrera and Nwaubani [133] investigated the behaviour of PC and MK pastes when subjected to sodium chloride in a standard diffusion cell. They discovered that the diffusion rates of chloride ions in these pastes were lower than those in the control mixtures. The expansion of MK mortar bars due to the action of sulphates was studied by Khatib and Wild [96]. The experiment involved immersing mortar samples in a 5% $Na_2SO_4$ solution for 520 days. Two types of cement were used, varying amounts of C3A and a range of MK replacements of up to 25%. The tests revealed that adding MK significantly decreased the expansion, which was further reduced as MK content increased. Mortar specimens containing MK concentrations of up to 10% exhibited a decrease in strength, while those with MK concentrations exceeding 15% demonstrated an increase in strength. The study suggested that the primary factor contributing to the improved sulphate resistance with MK was reduced CH content. The authors recommended a minimum of 15% cement replacement with MK to achieve good sulphate resistance. After 520 days, the expansion stopped at 20% and 25% MK replacement.

According to Martin [134] using MK in concrete can increase its durability when exposed to organic acids from silage effluents. By replacing 15% of the cement with MK, the concrete experienced a 30% reduction in mass loss when exposed to silage effluent. Another study by Pera et al. [135] investigated the effect of MK on the resistance of concrete to lactic acid and ammonium sulphate solutions, simulating an aggressive agricultural environment. The research showed that adding 10% MK reduced the damage caused by exposure to lactic acid. However, MK was less effective in the more aggressive ammonium sulphate solution than SF, although it displayed greater pozzolanic properties.

According to Usman and Sam [136] the ternary cement mortar containing palm oil fuel ash (POFA), MK and cement had a higher resistance to sulphuric acid attack in terms of their mass loss and compressive strength compared to binary blend mortars of POFA and cement. Al-Hashem et al. [137] reported that the concrete samples exposed to a 2% sulfuric acid solution had an insignificant decrease in compressive strength at 56 days compared to non-acid-attacked concrete, but at 90 days, the acid-exposed concrete had significantly lower compressive strength than the non-acid attacked concrete.

### *iii* ***Carbonation***

The incorporation of supplementary cementitious materials (SCMs) into concrete has been shown to reduce the rate of $CO_2$ ingress and carbonation depth [126,138] but also leads to lower alkalinity due to the consumption of calcium hydroxide (CH), which can increase carbonation depth. The effect of SCMs on carbonation kinetics depends on whether CH consumption or the lowering of alkalinity is dominant [126]. However, the presence of SCMs usually results in a greater carbonation depth [80,139], which is primarily attributed to the consumption of CH [140–143] and the decrease in pH from approximately 12.6 to less than 11 [144]. Despite this, the use of SCMs in concrete is generally permitted for most exposures as it meets the requirements of EN 206-1 and EN 197-1, except when the concrete is exposed to environments with high $CO_2$ concentrations.

Bucher et al. [145] investigated the relationship between accelerated and natural carbonation. They found a weaker correlation in concrete containing SCMs because of the slower reaction rate, and the curing duration had a crucial role in this effect. According to them, the incorporation of limestone filler and 15% MK showed exceptional resistance to carbonation, exhibiting a carbonation depth almost identical to that of the control samples.

In a study by Meddah et al. [120], accelerated carbonation was performed on pastes containing MK and SF. The results indicated that samples containing a higher amount of supplementary cementitious material (SCM) exhibited greater carbonation depth, thus confirming the significant impact of the W/C ratio on carbonation depth. Similarly, Jones et al. [146] reported that pastes containing both MK and FA demonstrated higher carbonation depth. However, Bakera and Alexander [126] found that specimens with 15% MK and a W/C ratio 0.5 showed 15% less carbonation depth after 90 days at 2% $CO_2$, 20±3ºC, and 65±5% relative humidity (RH). Other studies [147,148] also concluded that blends containing MK exhibited the same or less carbonation depth.

Barbhuiya et al. [125] conducted an experiment where concrete was subjected to accelerated carbonation for three weeks at 50.1% $CO_2$, 20.1°C, and 65.1% relative humidity. The study found that incorporating up to 10% of MK in the concrete did not significantly affect carbonation depth. Several studies have demonstrated that the W/C ratio has a greater impact on carbonation depth than any other factor [120,125,126,149]. Bakera and Alexander [126] found that at 0.4 W/B, the carbonation depth was negligible in the concrete samples irrespective of the MK replacement level from 0 to 20%; however, at 0.6 W/B, the carbonation depth was the same as that in the control sample. Wet curing time was also found to significantly impact the carbonation rate in blends that contain SCMs.

In their study, Mejia de Gutierrez et al. [150] conducted accelerated carbonation tests on various samples. The samples, which contained four different types of MK at a concentration of 10%, were wet-cured for 28 days and exposed to 2.25% $CO_2$ concentration at 30 °C and 70% RH. The carbonation depth was higher in the samples containing MK than in those with OPC. However, as the curing time increased to 240 days, the carbonation rate in all MK-containing samples slowed down.

### 2.1.5 Thermal resistance

Elevated temperatures induce significant alterations in the behaviour of concrete. As the temperature ascends, the water on the concrete surface and capillary water initiate evaporation due to augmented evaporation rates caused by weakened cohesive forces among water molecules. Hager [151] explained that the expansion of water accelerates this evaporation process. The residual strength of the concrete is contingent not only on the temperature but also on the duration of exposure [152].

Arslan et al. [153] observed a consistent decline in residual compressive strength when subjected to temperatures up to 900°C in MK blended mortars, increasing MK replacement level from 5% to 20%. Morsy et al. [154] found that a 20% replacement of cement with 10% MK and SF exhibited the highest residual compressive strength in mortar when heated up to 800°C. However, at 30% cement replacement, the combination of 5% MK and 35% SF demonstrated the highest residual compressive strength. Adding a 1% volume fraction of steel fibres increased the residual compressive strength at extreme heat of 800°C in 10% MK concrete [155]. When concrete is exposed to elevated temperatures, its strength diminishes due to the spalling effect and subsequent deterioration [156]. The addition of fibres minimises the cracking of concrete, causing increasing its strength. Poon et al. observed significant strength loss and increased permeability in MK-incorporated concrete samples compared to SF, FA, and OPC concrete after exposure to 200°C. The MK samples experienced explosive spalling, and the frequency of spalling rose with the MK content [154].

According to Wang et al. [157], incorporating 10% MK exhibited better thermal resistance, reduced shrinkage and a dense concrete microstructure compared to pure cement paste. However, Poon et al. [158] observed significant strength loss and increased permeability in MK-incorporated concrete samples compared to SF, FA, and OPC concrete after exposure to 200°C. The MK samples experienced explosive spalling, and the frequency of spalling rose with the MK content. This spalling phenomenon can be attributed to the vapour pressure formed within the compact pore structure of MK concrete. In a study by Abdelmelek and Lubloy [159], SF concrete exhibited superior temperature resistance compared to MK and FA concrete. The influence of MK and ground pumice (GP) on the interfacial structure between aggregates and cementitious matrix diminished as the temperature rose [160]. Nadeem et al. [161] also reported that the pore volume fraction at MK and FA concrete's interface transition zone (ITZ) increased with temperature. However, this study found that the residual compressive strength increased with an increase in MK dosage of up to 20%, with MK concrete outperforming FA concrete.

## 2.2 Nano-silica

Nano-silica (NS), silica nanoparticles, or silicon dioxide nanoparticles can be used as additives to improve concrete’s mechanical and durability properties [34,162,163]. The effect of NS on the nanostructure of cement paste also confirmed the concrete durability improvement [164]. The results revealed that NS is an excellent alternative to reducing cement consumption in high-strength concrete (HSC) [165]. Using NS as a cement replacement makes concrete more cost-effective and reduces the $CO_2$ footprint of concrete products [166]. Due to their improved performance in filling effect and particle size distribution, thereby decreasing the porosity in concrete and increasing their pozzolanic reaction with calcium hydroxide (Ca $(OH)_2$ or CH) to yield CSH, NS has gained particular attention in comparison with conventional minerals admixtures [167,168]. Such behaviours of NS resulted in improved mechanical properties in the concrete mix [169–171]. The cement setting process was enhanced by NS compared to silica fumes (SF) [172] bleeding and segregation decreased, and the cohesiveness of fresh mixes [173]. Nano-silica facilitates the hydration of cement at a very early age, and it can consume and convert CH into CSH gel due to its high pozzolanic action, thus enhancing the concrete's mechanical properties [174].

### 2.2.1 Effect of NS on mechanical properties of mortar/concrete

#### *i* *Compressive strength*

According to a set of investigations [171,175–183], even a minimal dosage of NS in concrete during its early stages can substantially impact compressive strength. The optimum NS dosage for strength enhancement was 2% to 3% replacement [171,174–176,179,182,184–186]. It was further observed that NS with smaller particle sizes demonstrates higher strength in the early stages of concrete development than larger particles [175].

Naji Givi et al.'s study [187] disclosed that NS with an average particle size of 15 nm heightened concrete strength in the early stages, while 80 nm NS particles demonstrated superior compressive strength at 90 days. Another investigation by Belkowitz et al. [188] observed that larger NS particles in cement composites significantly improved compressive strength and elastic modulus by over 20% compared to reference mixtures. The study also noted a 20% increase in compressive strength with the lowest doses of the smallest (5 nm) NS particles but a 14% reduction in strength at higher doses, suggesting that an excess of small NS particles may lead to the formation of agglomerated sites and voids, resulting in reduced strength.

The degree of agglomeration of NS particles determines the increase or decrease of concrete compressive strength, as Elkady et al. reported. [189]. Li et al. [190] discovered that achieving uniform dispersion of NS particles (10 ± 5 nm size) in concrete, particularly at higher dosages, posed challenges, resulting in weak zones within the concrete structure. Notably, concrete with 1% NS exhibited higher compressive strength than its 3% NS counterpart, suggesting that the agglomeration of small NS particles might have contributed to creating these weakened zones. Additionally, the study highlighted the poor workability observed at higher NS doses, leading to the development of microcracks in the concrete. In contrast, Nasution et al. [191] reported an increase in the compressive strength of concrete with an escalating NS content reaching up to 10%.

Elkady et al. [192] documented a 13.5% increase in compressive strength at 7 days when 4.5% NS was added to concrete. Meanwhile, dosages of 1.5% and 3% NS resulted in strength gains of 3% and 4.5%, respectively, compared to the control specimen. At 28 days, strength gains were further observed, with percentages of 43.5% at 3% NS and 17.5% and 29% at 1.5% and 4.5% NS dosages, respectively. The study attributed these strength gains to the agglomeration of NS particles, which prolonged the time required for their reaction with excess CH to form CSH gel. The agglomerated NS particles, acting as filler materials, reduced porosity, enhancing early-age strength. Additionally, the optimal 3% NS dosage significantly improved bond strength by 38.5% compared to the control sample.

Singh et al. [162] noted a significant enhancement in the early-age compressive strength of nano-engineered fly ash concrete with the addition of NS particles. The effectiveness of NS particles was particularly pronounced at 3 days compared to 7 and 26 days, indicating their role in promoting the early hydration process of cement. Findings from studies [34,163] propose that NS particles accelerate the early hydration rate and increase the packing density of CSH, transitioning from low to high.

The research conducted by Chithra et al. [193] reported that high-performance slag concrete (HPSC) containing 2% NS exhibited high CSH at early ages, resulting in a remarkably compact structure. This denser CSH formation contributed to heightened early strength. However, as time progressed, the presence of NS particles in the concrete reduced porosity, hindering further hydration processes [194]. A recent investigation into NS concrete [195] indicated that the increased early-age compressive strength can be attributed to the high pozzolanic activity of NS during the initial stages. Conversely, the increase in 28-day compressive strength is ascribed to the filling of voids by the formed CSH gel and the improved bonding between mortar and aggregates. The smaller and finer NS particles effectively fill the gaps between cement grains, contributing to the overall strength development [196].

Introducing 2% NS in dolomite concrete resulted in increased compressive strength, while a 4% NS dosage reduced strength [197]. Fallah et al. [198] noted that including macro-polymeric and polypropylene fibres, with 2% and 3% NS, respectively, elevated the compressive strength in high-strength concrete. Furthermore, the combination of 3% NS and 0.2% polypropylene exhibited a 13.5% strength increase compared to plain concrete. The mechanical properties of self-compacting concrete (SCC) admixed with ground granulated blast furnace slag (GGBFS) improved with the addition of up to 3% NS particles [199]. Nevertheless, higher NS dosages (>3%) decreased strength due to reduced crystalline CH content essential for CSH gel formation. The incorporation of 0.5% to 1% NS into ground ceramic powder concrete mitigated the adverse effects of ground ceramic powder on concrete's mechanical properties, as observed by Heidari et al. [200].

During the early stages, the heightened reactivity of NS with CH generated during the hydration process led to increased compressive and tensile strengths in high-performance self-compacting concrete (HPSCC). This acceleration in hydration resulted in a substantial amount of reaction products and subsequent strength development [184]. The evaporation rate in SCC containing smaller NS particles induced large open porosity at 7 days, but the high pozzolanic activity increased the strength at 28 days [201]. Hameed et al. [202] observed a significant increase in compressive strength of 48% in SCC with an elevated colloidal NS (CnS) content compared to the reference concrete at 28 days. Massana et al. [203] noted a consistent increase in compressive strength with the addition of NS up to 7.5% in HPSCC, resulting in a 13% increase at 28 days compared to the reference mix. The study also revealed that the combined use of 2.5% NS and mS (micro-silica) led to the highest increase in compressive strength (31%), attributed to the chemical synergy effect [165] and improved packing of concrete particles.

In SCC, NS exhibited superior compressive strength compared to powdered NS across all test stages from 3 to 91 days [204]. However, the reference concrete demonstrated higher strength on the first day than NS concrete. Puentes et al. [201] also reported lower strength in NS-incorporated SCC at one day but higher strength at 28 days. Adding NS solution to the concrete mix moderately enhanced strength after 28 days compared to an equivalent amount of powdered NS, but it did not improve early strength [205].

Alhawat et al. [180] observed that the rapid hydration facilitated by nano-silica (NS) led to the formation of abundant hydration products, resulting in increased density and homogeneity of concrete [176]. The micro cement particles were effectively filled by silica nanoparticles, contributing to a more condensed structure [206]. Du et al. [207] observed that the early-age strength of lightweight concrete (LWC) improved due to the high hydration rate in the presence of NS particles. However, this strength gain diminished with prolonged curing. In self-compacting lightweight aggregate concrete (SCLC), higher 28-day compressive strength was evident at NS replacement levels up to 5% for water-binder (w/b) ratios of 0.25, 0.37, and 0.5 [208]. Adding 3% NS to high-strength lightweight concrete (HSLWC) alleviated the adverse effects of coarse lightweight aggregate, significantly enhancing the mechanical properties of the concrete [196]. Elrahman et al. [177] also noted a rise in compressive strength in LWC with NS up to 4%.

Several investigations have shown that incorporating NS into concrete markedly improves its compressive strength, particularly in the early stages. The optimum NS dosage falls within the 2% to 3% range. Smaller NS particles generally exhibit higher early-age strength, though particle size can impact strength development in later stages.

NS particle agglomeration can create weak zones, affecting workability and reducing strength. Conversely, uniform dispersion of NS particles enhances both strength and workability. NS accelerates the early hydration rate, speeds up hydration product formation, and alters the packing density of calcium silicate hydrate (CSH). The positive impact of NS on compressive strength is observable in various concrete types, including fly ash concrete, slag concrete, dolomite concrete, high-strength concrete, self-compacting concrete, lightweight concrete, and lightweight aggregate concrete. Careful control of NS dosage and particle size is crucial to achieving desired strength improvements while avoiding potential drawbacks such as agglomeration and reduced workability.

#### *ii* ***Tensile strength, flexural strength and modulus of elasticity***

Several investigations demonstrated that incorporating NS in concrete increased tensile strength compared to ordinary and mineral admixed concretes. Hasan-Nattaj et al. [209] observed an 8.2% and 80.6% rise in tensile strength for steel-fibre reinforced concrete with 2% NS compared to fibre-reinforced and plain concrete, respectively [209]. Adding NS significantly elevated the splitting tensile strength in HPSCC [184]. Naji Givi et al. [187] noted heightened compressive, tensile, and flexural strengths compared to non-NS concrete, particularly pronounced for 80 nm particles. Moreover, NS incorporation reduced voids in the mortar matrix, enhancing the ITZ and subsequently increasing split tensile strength [195]. Introducing 3% NS in polyethylene terephthalate (PET), composite concrete resulted in a 25% increase in tensile strength relative to the reference concrete [186].

The inclusion of NS in concrete was found to augment flexural strength. When NS was used in HPSCC with silica fume (SF), the flexural strength saw a maximum improvement of 59% at 28 days [184]. Naji Givi et al. [187] reported that NS particles enhanced flexural strength at all curing stages up to 90 days, with 80 nm particles displaying superior strength compared to 15 nm particles. NS also improved adhesion between cement paste and aggregate in PET composite concrete, increasing flexural strength [186]. Furthermore, doses of NS above 1% effectively heightened flexural strength at 28 days in lightweight aggregate concrete (LWAC) [177].

The addition of NS significantly impacted the elastic modulus of concrete. NS concrete exhibited higher stiffness than non-NS concrete, indicating a higher elastic modulus [210]. The densification of the interface between aggregates and the cement matrix through NS addition strengthened their bond, increasing stiffness [211]. However, the increase in elastic modulus was influenced by the size of NS particles and their surface area, with smaller particles generating a higher modulus and larger particles exhibiting a stronger effect at higher doses [188]. Additionally, NS was observed to enhance the compactness and density of concrete, thereby improving the elastic modulus [195]. The optimal elastic modulus was observed at 2.5% NS content in SCC [202]. Notably, the elastic modulus of concrete with 25% fly ash alone was comparable to that of concrete with 2% NS and 25% fly ash [206].

### 2.2.2 Effect of NS on durability properties of mortar/concrete

#### *i* ***Water absorption sorptivity, water permeability and infiltration rate***

Ghafari et al. [176] found that adding NS reduced water absorption and sorptivity in UHPC compared to the reference concrete mix. This indicates a significant decrease in the connection between capillary pores due to the pores being filled with additional hydration products formed by the high pozzolanic reactivity of NS. Similar effects were observed by Du et al. [207], who noted a 35% reduction in the initial setting time and a 32% reduction in secondary sorptivity in pure cement LWC with the addition of 2% NS. This was considered an optimum dose for pure cement as an additive. However, in slag cement LWC, the initial and final sorptivity was reduced to 73% and 83%, respectively, using 1% NS, considered an optimum dose for slag cement. This reduction could be attributed to the insufficient densifying effect of NS at higher dosages, failing to compensate for the increased air content and subsequent development of more pores in hardened concrete. According to Atmaca et al. [196], the sorptivity of 3% NS HSLWC decreased by 25% compared to the reference concrete with the same level of LWA replacement. Elrahman et al. [177] reported a beneficial effect of 4% NS on LWC, reducing porosity and water absorption. In hardened high-strength concrete with macro-polymeric (MP) and polypropylene (PP) fibres, the presence of NS was found to reduce water absorption, with the least value observed at 3% NS [198]. Younis et al. [212], an 11% decrease in water absorption in RAC with a small NS dosage of 0.8% compared to control concrete was observed.

Isfahani et al. [213] found that 0.5% NS, as a cement replacement, had a negligible effect on water absorption and sorptivity in concrete with a 0.65 w/b ratio. However, an apparent reduction was observed at a 0.55 w/b ratio with 1% NS. Kumar et al. [174] reported a 36.84% decrease in water absorption in concrete with 3% NS compared to normal concrete, attributing it to the highly reactive NS forming more CSH gel and packing the voids of the concrete matrix.

The permeability decreased with an increased NS dosage, reaching a maximum reduction of 51.5% compared to the control mix at 4.5% NS [192]. Erdem et al. [214] reported a similar effect of NS in RAC, improving its porous structure. Rezania et al. [215] noted a decreasing trend in permeability reduction with an increase in nanoparticle content, attributed to the difficulty of their dispersion in concrete at higher dosages. In alkali-activated slag (AAS) concrete, using NS led to an undesirable rise in water penetration depths, while using mS reduced permeability [216].

Compared to concrete containing NS, the decrease in water absorption in fibre-reinforced concrete with SF was more noticeable, according to Hasan-Nattaj et al. [209]. Conversely, Jalal et al. [184] showed that water absorption in HPSCC was further reduced by including 2% NS with 10% SF, achieving efficient packing and refinement of concrete micro and pore structures through the combined effect of NS and SF. Due to its more refined pore structure, water absorption in concrete with NS was reduced by 6.4% and 18.3% compared to concrete with mS and reference concrete [217].

Najigivi et al. [218] reported that rice husk ash (RHA) mixed concrete with 15 nm NS significantly enhanced water absorption resistance at 28 days, while higher resistance was observed in concrete with 80 nm NS after 90 days. Tawfik et al. [219] found the lowest water penetration in HPC containing 3% NS compared to HPC with silica fume, fly ash, or coal nanoparticles. Mohammed et al. [220] reported that NS particles induced fly ash reaction, decreasing the roughness of the inner surface of the voids, resulting in increased infiltration in the previous concrete as for an excellent pervious concrete, a better infiltration rate is favourable.

### *ii* ***Aggressive environment***

The specimen incorporating NS and exposed to sulfuric acid rain demonstrated a higher compressive strength than the control specimen, attributed to the reduced porosity resulting from the filling effect of NS and the enhanced bonding between aggregates and hydrated cement paste in the presence of NS [221]. As the NS content increased in acid exposure, the weight loss percentage in concrete specimens decreased. In contrast, the electrical resistance increased due to greater compactness and changes in pore solution composition caused by NS.

However, [222] reported that in high-strength forta-ferro fibre (HSFF) concrete, the use of SF showed superior durability compared to NS when exposed to an acidic environment. The HSFF concrete specimen with 2% NS exhibited a substantial reduction in ultrasonic pulse velocity (UPV) compared to specimens with 10% SF during a 63-day immersion in sulfuric acid. Additionally, the study demonstrated lower weight loss in specimens with a high replacement level of 10% SF, indicating less erosion in acid exposure compared to the low replacement level of 2% NS. This result was attributed to the lower potential for gypsum and ettringite production in concrete specimens containing 10% silica fume. Moreover, the higher SF replacement level, relative to the lower NS replacement level, resulted in a greater crushing load loss to weight loss ratio.

Concrete specimens containing 3% NS immersed in sewage water for 90 days exhibited the least reduction in compressive strength due to sulphate attack, suggesting that NS particles are highly effective in resisting sulphate attacks in concrete [220]. This indicates that the NS particles are very effective in resisting sulphate attacks in concrete.

#### *iii* ***Carbonation***

Singh et al. [162] found that incorporating 3% NS in FA concrete significantly diminished carbonation depth by 73% after 180 days of exposure compared to the control mix. In contrast, FA concrete with SF exhibited only a 35% reduction under the same conditions. This outcome is attributed to the stability and resistance of hydration products formed in the presence of NS, indicating the potential for enhanced durability in FA concrete. Kumar et al. [174] noted a 46% and 17% decrease in carbonation depth at 7 and 70 days, respectively, with up to 3% NS in ordinary concrete. However, further NS additions increased carbonation depth over time, potentially due to excess CH reacting with NS to form CSH gel. A dense matrix was achieved at the 3% NS dosage, and additional NS did not contribute to further densification.

Isfahani et al. [213] observed a detrimental impact on carbonation with NS addition, with the carbonation coefficient increasing from 24 to 29.3 mm/year at 1% NS for a 0.65 w/b ratio. Conversely, at the same NS level but with a 0.55 w/b ratio, the carbonation coefficient decreased from 20.4 to 16 mm/year. Behfarnia et al. [216] reported increased carbonation depth in AAS concrete with NS particles, attributing it to heightened $CO_2$ penetration.

### 2.2.3 Thermal resistance

Elkady et al. [192] reported an initial reduction in compressive strength of around 30, 16, 25, and 22% during the indirect fire test at temperatures ranging from 0°C to 400°C, corresponding to 0, 1.5, 3, and 4.5% NS content, respectively. Nevertheless, these declines escalated to 49, 27, 37, and 62% within the temperature span of 400°C to 600°C. Within the temperature range of 0°C to 400°C, the test specimens exhibited a reduction of approximately 37, 29, 49, and 26% in their initial bond strength at NS dosages of 0, 1.5, 3, and 4.5%, respectively. Conversely, during the temperature interval of 400°C to 600°C, the corresponding strength reductions were approximately 84, 65, 79, and 86%. The research proposed that the initial strength loss at temperatures between 0°C and 400°C resulted from the decline in cohesive force among the layers of CSH gel, while at higher temperatures (400°C to 600°C), the loss of strength was linked to the development of severe vapour pressure within the dense pores, leading to concrete spalling and cracking.

In the temperature range of 110-650°C, the thermogravimetric analysis conducted by [199] revealed dehydration of the hydrated products and an increased weight loss after a 90-day curing period in specimens with NS particles up to 3% in GGBFS-incorporated SSC. The occurrence of spalling and mass loss in NS-admixed HSC was observed when the temperature exceeded 400°C, whereas this phenomenon was noted just above 300°C for HSC without NS [224].

## 2.3 Summary

MK is a highly valuable natural pozzolan to concrete formulations, enhancing mechanical and durable properties. Its filler effect, acceleration of cement hydration, and high pozzolanic reaction improve concrete mechanical properties, with optimal replacement levels typically ranging from 10% to 20% MK replacement. MK's impact on fresh concrete properties varies, influencing workability, setting times, and water demand. The inclusion of MK positively affects the durability of concrete, reducing water absorption, enhancing resistance to aggressive environments, and mitigating carbonation effects. Additionally, MK contributes to improved thermal resistance, although the extent varies with dosage and exposure conditions. The overall findings emphasise MK's potential as a sustainable and performance-enhancing material in concrete applications.

Due to its high surface area, NS is a promising additive that enhances concrete mechanical and durability properties. NS reduces cement consumption in high-strength concrete, making it cost-effective with a reduced $CO_2$ footprint. It improves compressive strength, with an optimal dosage of 2-3%, smaller particles demonstrating higher early-age strength. NS also enhances tensile and flexural strengths, adhesion, and elastic modulus. In terms of durability, NS reduces water absorption, sorptivity, and permeability, enhancing resistance to aggressive environments like acid exposure and sulfate attacks. Notably, NS mitigates carbonation effects and contributes to thermal resistance, although caution is needed with high temperatures. Achieving optimum NS dosage and particle dispersion is critical for maximising benefits while addressing potential drawbacks.