Chapter 4

Results and Discussions - Mortar

4.1 Introduction

This chapter presents a comprehensive investigation into the compressive strength of mortars containing ternary and binary combinations of MK and NS, utilised as partial replacements for cement. The MK dosages were varied at 10%, 15%, and 20%, while NS dosages were introduced at 1%, 3%, and 4.5%. The reference sample of cement unary mix was also prepared for comparative analysis, as discussed in the previous chapter.

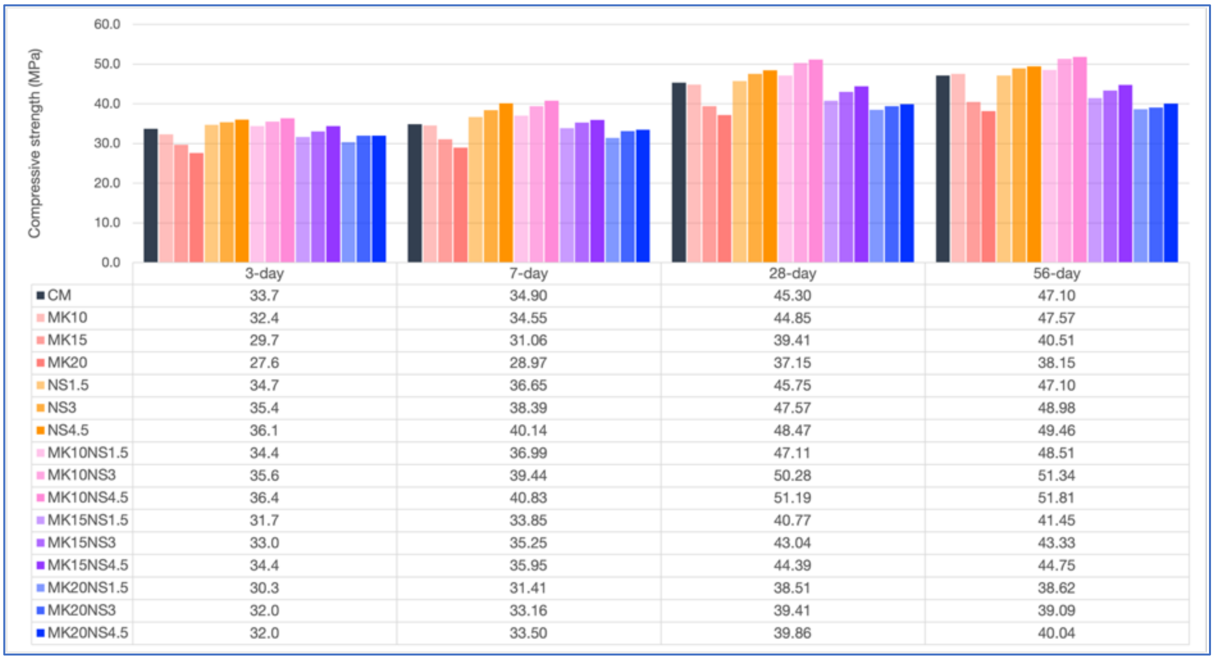
The main objective of this study was to assess the relative strength of each mortar combination concerning the reference sample. The compressive strength tests were meticulously conducted, and the results provided valuable insights into the influence of MK and NS dosage on the compressive strength of mortars. Moreover, the pozzolanic efficiency factor (k-factor) was calculated to quantify the contribution of MK and NS to the overall strength development. The mortar test results were pivotal in determining the suitable mix compositions and proportions for concrete, considering strength enhancement.

To gain insights into the strength development and microstructural changes, thermogravimetric analysis (TGA), X-ray diffraction (XRD), and scanning electron microscopy (SEM) were conducted. These analytical techniques offer valuable information about the hydration products and microstructural characteristics of the developed mortars

The subsequent sections of this chapter delve into the detailed presentation and analysis of the test results, along with the discussions on the implications of the findings.

4.2 Compressive strength

The variations in compressive strength among binary and ternary compositions of MK and NS mortar relative to the reference mortar (CM) are shown in Figure 4.1. Compressive strength development in various MK and NS mortar compositions is analysed in greater detail in subsequent sections.



	3-day	7-day	28-day	56-day
■ CM	33.7	34.90	45.30	47.10
■ MK10	32.4	34.55	44.85	47.57
■ MK15	29.7	31.06	39.41	40.51
■ MK20	27.6	28.97	37.15	38.15
■ NS1.5	34.7	36.65	45.75	47.10
■ NS3	35.4	38.39	47.57	48.98
■ NS4.5	36.1	40.14	48.47	49.46
■ MK10NS1.5	34.4	36.99	47.11	48.51
■ MK10NS3	35.6	39.44	50.28	51.34
■ MK10NS4.5	36.4	40.83	51.19	51.81
■ MK15NS1.5	31.7	33.85	40.77	41.45
■ MK15NS3	33.0	35.25	43.04	43.33
■ MK15NS4.5	34.4	35.95	44.39	44.75
■ MK20NS1.5	30.3	31.41	38.51	38.62
■ MK20NS3	32.0	33.16	39.41	39.09
■ MK20NS4.5	32.0	33.50	39.86	40.04

Figure 4.1 Compressive strength of mortars

4.2.1 Compressive strength of binary blended mortars with replacement by MK

Figure 4.1 illustrates that replacing OPC with MK reduced the compressive strength of the mortar as the MK weight percentage increased from 10% to 20%. MK10 had a high compressive strength among the binary blends of MK but slightly less than CM at 28 days. Meanwhile, MK15 and MK20 had 13% and 18% lower strength than the CM, respectively. At 3, 7, and 28 days, the compressive strength of MK10 was slightly lower than that of the CM by 4%, 1%, and 0.99%, respectively, but displayed slightly higher strength at 56 days. The cube strength of the CM was 45.3 MPa and 47.1 MPa at 28 and 56 days, respectively, while the MK10 mortar exhibited strengths of 44.9 MPa and 47.6 MPa at the same ages. This suggests a continued pozzolanic reaction of MK particles with CH at later ages. The difference in strength between the MK10 and the CM decreased as the curing age increased, but this trend was reversed in the MK15 and MK20 mortars.

The incorporation of MK powder, characterised by its high specific surface area (SSA), causes a substantial increase in pozzolanic active surface area, exceeding that of cement particles multiple times. The pozzolanic reaction happens on the surface of MK particles, and its progression necessitates a continuous supply of Ca^{2+} cations, one of the hydration products of cement. The speed of the pozzolanic reaction is limited by the alite hydration rate and the Ca^{2+} cations diffusing to the surface of MK particles. However, at high MK dosages of 15 and 20 wt.%, the rate of cement hydration is inadequate to facilitate a pozzolanic reaction on the surface of MK particles. Consequently, a notable proportion of unreacted MK, which did not undergo the pozzolanic reaction and did not produce hydrates in the form of CSH and calcium aluminosilicate hydrates (CASH), may remain in the volume of the cement-water matrix. As a result, the unreacted MK, at high replacement levels of 15 and 20%, can cause a reduction in compressive strength. It is worth noting that replacing mineral admixtures at high levels does not significantly affect the hydration process, as evidenced by previous studies [235]. Figure 4.2 illustrates the correlation between compressive strength and the MK/B ratio. The optimal replacement rate for MK in the mortar was thus found to be 10%, in agreement with previous studies on concrete with MK substitution [33,236]

On the other hand, according to a study conducted by Poon et al. [158], replacing 10% of MK reduced only 70% in CH content. Moreover, the replacement of 20% led to a near elimination of CH within 28 days. Nonetheless, achieving complete CH removal through MK substitution relies on MK purity, Portland cement composition, weight-to-volume ratio, and curing conditions [237].

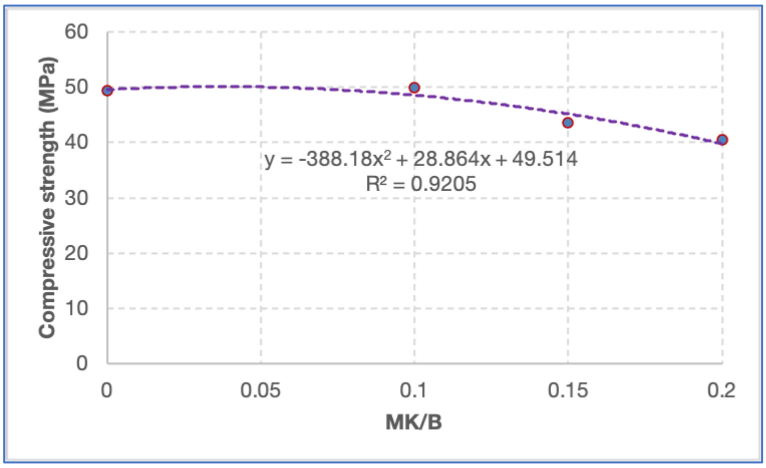


Figure 4.2 Correlation between MK/B ratio and 28-day compressive strength in MK binary blended mortars.

4.2.2 Compressive strength of binary blended mortars with replacement by NS

Mortar compressive strength had an incremental effect at all ages when up to 4.5% of the OPC was replaced with NS, as shown in Figure 4.1. Compared to the CM, the compressive strength of the NS 1.5, 3, and 4.5% binary blended mortars increased by 1, 5, and 7% after 28 days. NS1.5 and NS3 binary mortar had strengths of 45.8 MPa and 47.6 MPa at 28 days, respectively, while the NS4.5 mortar demonstrated strength of 48.5

MPa. The NS1.5 binary composite mortar's strength increased to 47.1 MPa after 56 days, while the NS3 and NS4.5 mortar's strengths were 49 and 49.5 MPa, respectively.

Mortars' compressive strength increased as the dosage of SiO_2 was raised, with the dependence closer to linear, as shown in Figure 4.3. SiO_2 nanoparticles, with a high SSA of 150 m^2/g and an average diameter of 18.1 nm, have a higher concentration in the cement-water matrix than MK particles. Therefore, the total surface area of the active pozzolan introduced by SiO_2 nanoparticles into the cement-water matrix is considerably greater than that of MK particles. Therefore, at SiO_2 dosages between 1.5 and 4.5 wt.%, the proportion of NS involved in the pozzolanic reaction is substantially high, increasing the volume of CSH and, consequently, the compressive strength of cement mortars.

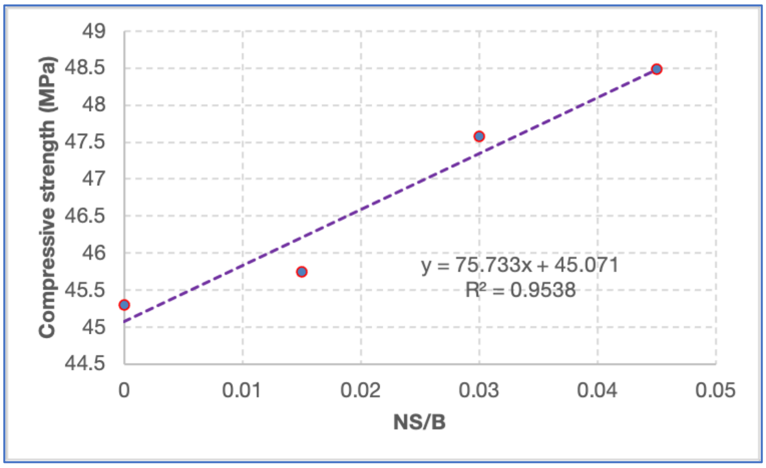


Figure 4.3 Correlation between NS/B ratio and 28-day compressive strength in NS binary blended mortars

To explain the increase in compressive strength with an increase in the dosage of NS, it is necessary, in addition to the pozzolanic effect, to take into account the effects of the influence of nanoparticles on the ordering of the CSH gel structure, an increase in the volume density of packing of gel nanogranules, and the effect of filler in the capillary and gel pores of the cement-water matrix.

4.2.3 Compressive strength of ternary mortars with replacement by MK and NS combinations

Adding MK and NS in ternary blends resulted in higher compressive strength than the binary blends of MK and NS. However, an increase in MK proportions reduced compressive strength, consistent with the findings observed in binary mixtures containing only MK. However, the compressive strength values were significantly higher than those in the MK15 and MK20 binary compositions without NS. With a constant MK dosage, the compressive strength increased with an increase in NS dosage, in a nearly linear relationship, as seen in Figure 4.4. Incorporating NS compensated for the reduction in compressive strength due to increased MK content, observed in MK15 and MK20 binary blended mortars, in ternary blended mortars containing a combination of MK and NS at doses of 15 and 20 wt.%. In all ternary compositions of 10% MK and NS, the compressive strength was greater than that of the binary blended mortar of MK10 and the CM at all ages. The highest compressive strength observed in ternary blended mortars at 28 days was 51.2 MPa for the MK10NS4.5 composition, with a slight increase to 51.8 MPa noted at 56 days. Compared to the CM, the ternary blend of MK10NS exhibited an improvement in strength of 4%, 11%, and 13% at 28 days and 3%, 9%, and 10% at 56 days for 1.5%, 3%, and 4.5% NS dosages, respectively. This can be explained by the fact that at a dose of MK 10 wt. %, a significant proportion of MK had time to enter into the pozzolanic reaction; the proportion of unreacted MK was relatively low, while the pozzolanic and structural effects of the NS were manifested.

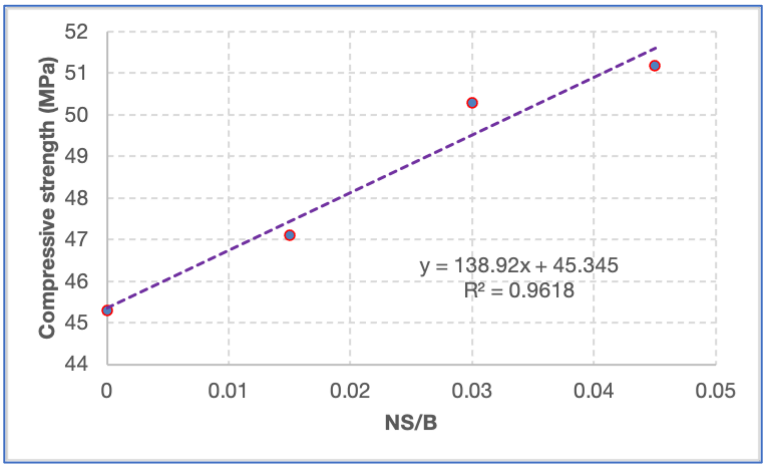
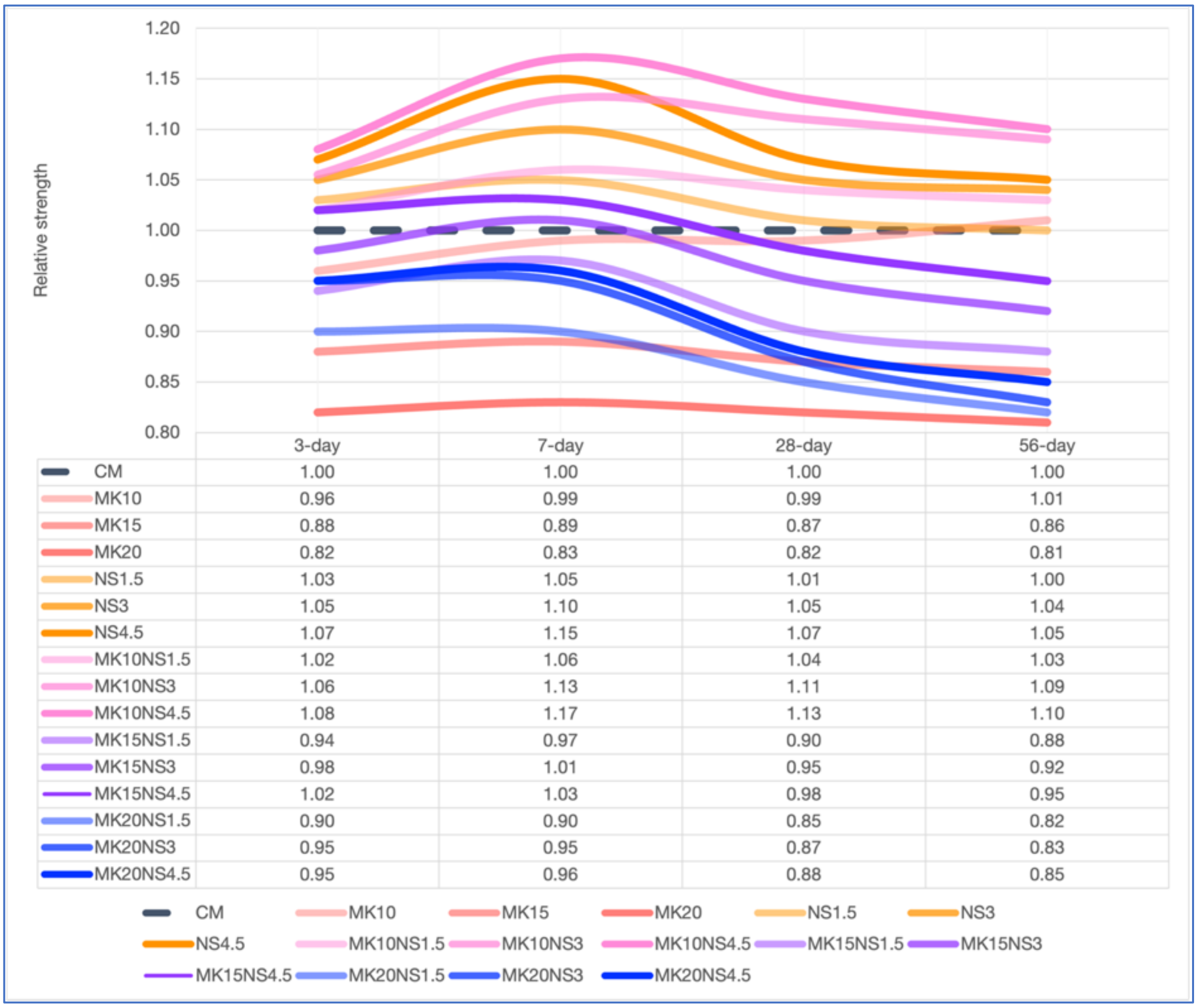


Figure 4.4 Correlation between NS/B ratio and 28-day compressive strength in MK10NS ternary blended mortars

The effects of MK on compressive strength can be attributed to the acceleration of alite hydration, acceleration of the kinetics of the pozzolanic reaction, and the polymerisation of silicon-oxygen tetrahedrons forming the CSH gel structure. The packing effect of MK can fill the interstitial voids in the hardened microstructure of cement mortar, increasing strength and density. The pozzolanic effect improves the bonding strength and solid volume by combining glass-like silicon and alumina in MK with calcium oxide and hydroxide in cement, thus increasing the cured mortar's compressive strength [30,158,238]. The compositions MK15NS and MK20NS exhibited significantly less strength than the CM. An increase in pozzolanic material does not result in a corresponding rise in hydration rate due to the decreased availability of CH for reaction. The incomplete reaction of MK, even after 90 days, suggests that roughly half of the MK remains unreacted at 10% and 20% replacement levels [235,239]. According to Nazari and Riahi [199], an increase in the replacement level of NS particles led to a decrease in strength. This was attributed to a reduction in the amount of crystalline CH necessary to form CSH gel.

4.3 Relative strength

Figure 4.5 illustrates the plots depicting the relationship between relative strength and curing age in days for various cement blends. This plot provides insight into the reaction rate within the blended cement system compared to the plain OPC system.



	3-day	7-day	28-day	56-day
CM	1.00	1.00	1.00	1.00
MK10	0.96	0.99	0.99	1.01
MK15	0.88	0.89	0.87	0.86
MK20	0.82	0.83	0.82	0.81
NS1.5	1.03	1.05	1.01	1.00
NS3	1.05	1.10	1.05	1.04
NS4.5	1.07	1.15	1.07	1.05
MK10NS1.5	1.02	1.06	1.04	1.03
MK10NS3	1.06	1.13	1.11	1.09
MK10NS4.5	1.08	1.17	1.13	1.10
MK15NS1.5	0.94	0.97	0.90	0.88
MK15NS3	0.98	1.01	0.95	0.92
MK15NS4.5	1.02	1.03	0.98	0.95
MK20NS1.5	0.90	0.90	0.85	0.82
MK20NS3	0.95	0.95	0.87	0.83
MK20NS4.5	0.95	0.96	0.88	0.85

Figure 4.5 Relative strength vs. curing time

Specifically, the binary blend mortar with 10% MK achieved a relative strength of 0.99 after 28 days. Notably, the relative strength of the MK 10 binary blended mortar exhibited a significant increase from 3 days to 7 days, followed by a gradual rise to 1.01 at 56 days.

The most substantial strength improvement in the blended mortars was observed between 3 and 7 days. This aligns with the findings of Wild et al. [30], who reported a maximum strength improvement in concrete with MK within the first 7 to 14 days. This improvement is attributed to the combined filler effect of the finer MK particles and accelerated cement hydration.

The pozzolanic reaction involving the silica and alumina content in the MK particles, along with the CH formed during cement hydration, contributes to the creation of a secondary CSH gel. This secondary CSH gel enhances the strength of MK blended binary mortar [240–243]. Figure 4.6. provides a schematic representation of the CSH formed by cement hydration and the secondary CSH formed by the pozzolanic reaction of MK and NS particles with CH.

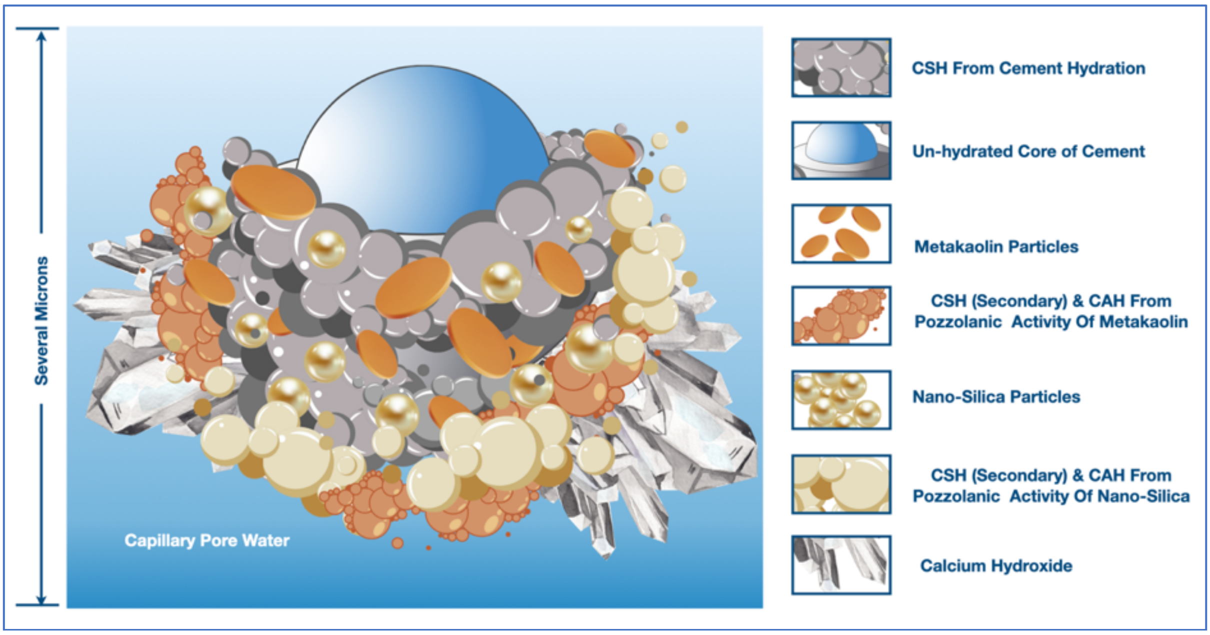


Figure 4.6 Schematic of cement hydration and pozzolanic activity of MK and NS particles, Abhilash et al. [244]

The reactivity of MK and other factors, such as their replacement levels, can also influence the hydration reaction rate. Thus, the complete removal of CH from concrete may require more than 28 days [245].

At 56 days, the relative strength of MK10 slightly reached 1.01, indicating a decrease in CH content at that age due to pozzolanic reaction, as shown in Figure 4.6. This aligns with the observations of Frías and Cabrera [64], who noted an inflexion point that represents the end of the pozzolanic reaction when MK is fully consumed, at 56 and 90 days for mixtures with 10% and 15% of MK, respectively. Beyond the inflexion point, the CH content increases again, leading to a reduction in strength. The change in CH content is attributed to different hydration mechanisms, with OPC hydration causing an increase and the pozzolanic reaction of MK causing a decrease.

In MK15 and MK20 binary blended mortars, it was evident that the relative strength consistently remained below 1 at all ages. Notably, the increased substitution with 15% and 20% MK might have reduced compressive strength over time due to a dilution effect on cement hydration [240].

For NS binary blended mortars, the relative strength exceeded or equalled 1 at all ages. Moreover, relative strength increased with an increase in NS replacement level from 1.5 to 4.5%, suggesting accelerated hydration attributed to more nucleation sites for the hydration process [171,175,187]. NS accelerates cement hydration by reacting with lime to create more CSH and acting as a catalyst to speed up hydration while reducing porosity through its filler effect [246]. The hydration process of NS blended mix and its resulting strength development are influenced by various factors such as particle size, NS quality, mix type, and water-to-binder ratio.

Figure 4.5 illustrates the noticeable characteristics of the binary NS4.5 mortars as they exhibited a remarkable early-stage relative strength, steadily increasing to 1.15 at 7 Subsequently, it experienced a decline, converging towards a relative strength of 1.05 at the 56-day mark. The early strength development can be attributed to the formation of ettringite, effectively filling the pores, as reported by Liu et al. [247]. The dilution effect within NS binary mortars is negligible, given that the percentage replacement of NS up to 4.5% is comparatively low.

Previous studies have reported increased early-age strength to the agglomeration of NS particles, which served as a filler material to reduce porosity and cause a slower reaction with excess CH to form CSH gel [192]. However, according to [195], the early-age increase in compressive strength may be attributed to the pronounced pozzolanic activity of NS. Meanwhile, the 28-day compressive strength rise is likely a result of void filling and the strengthening of mortar bonding through the formation of CSH gel. Various studies on the strength of NS-incorporated concrete have yielded diverse results. Some have observed heightened strength at early stages, while others note increased strength after 28 days [204,248,249], while Massana et al. [80,203] reported a steady increase in strength over time.

All ternary blends of MK10NS exhibited a relative strength value above 1 for 56 days. Notably, MK10NS4.5 demonstrated the highest relative strength value, although the disparity in relative strength values between MK10NS3 and MK10NS4.5 blends was minimal. However, exceptions were observed for MK15NS3, which showed a relative strength value above 1 at 7 days, and MK15NS4.5, with a value above 1 at 3 and 7 days. This phenomenon was attributed to increased pozzolanic reactivity in the presence of NS particles. Moreover, a high MK replacement resulted in a diminished rate of hydration due to the dilution effect. The maximum relative strength value, which corresponds to the minimum CH content, indicates the peak of pozzolanic activity [30].

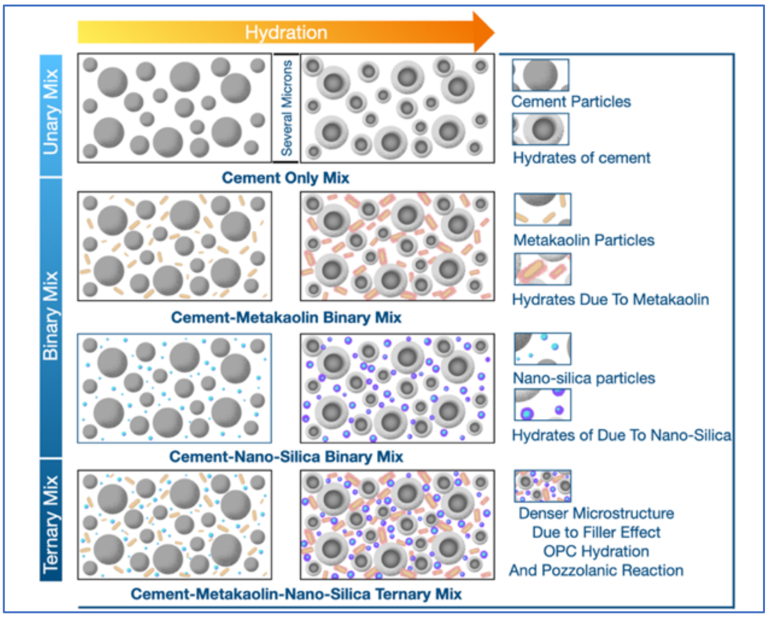


Figure 4.7 Schematic of the microstructure of cementitious materials for unary, binary and ternary blends of cement, MK and NS, Abhilash et al. [244]

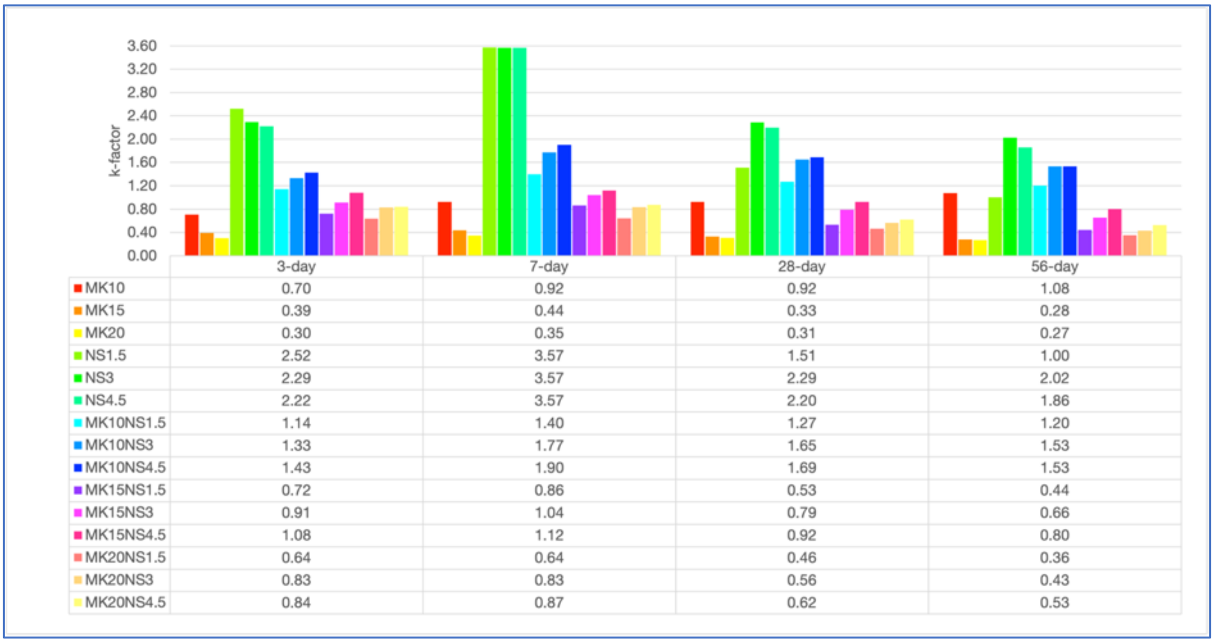
Figure 4.7 shows a schematic representation of the microstructure of cementitious materials for unary, binary and ternary blends of cement, MK and NS.

4.4 Pozzolanic efficiency factor

The pozzolan cementing efficiency factor, or k-factor for blended cement mortars comprising OPC, MK and NS combinations in binary and ternary formulations, was determined using the modified Bolomey equation 3.4. The k-factor quantifies the proportion of cement that can be substituted in the concrete mixture with one part of pozzolan while preserving the concrete's desired properties [227]. The k-factor of OPC is always 1 [229]. Therefore, the k-factor can be utilised to convert a specific quantity of pozzolan into an equivalent amount of cement in terms of strength contribution.

Bolomey coefficient 'A' calculated from the equation 3.2 for 3, 7, 28 and 56-day strength of reference mortar were 20.13, 20.85, 27.06 and 28.14, respectively.

The variations in k-factor, calculated in terms of compressive strength, for MK and NS binary and ternary blended cement mortars are shown in Figure 4.8. It was observed that there was no singular k-factor for a specific blended cement mortar existed as it varied with curing age. In all the cases, the k-factor of the blends were high at 7 days and then slowly decreased till 56 days.



	3-day	7-day	28-day	56-day
MK10	0.70	0.92	0.92	1.08
MK15	0.39	0.44	0.33	0.28
MK20	0.30	0.35	0.31	0.27
NS1.5	2.52	3.57	1.51	1.00
NS3	2.29	3.57	2.29	2.02
NS4.5	2.22	3.57	2.20	1.86
MK10NS1.5	1.14	1.40	1.27	1.20
MK10NS3	1.33	1.77	1.65	1.53
MK10NS4.5	1.43	1.90	1.69	1.53
MK15NS1.5	0.72	0.86	0.53	0.44
MK15NS3	0.91	1.04	0.79	0.66
MK15NS4.5	1.08	1.12	0.92	0.80
MK20NS1.5	0.64	0.64	0.46	0.36
MK20NS3	0.83	0.83	0.56	0.43
MK20NS4.5	0.84	0.87	0.62	0.53

Figure 4.8 Pozzolanic efficiency factor (k-factor) of mortar blends at various curing ages

The MK10 binary blend achieved higher efficiency (k-factor) than 1 at 56 days. Additionally, it was observed that the efficiency of MK blended cement mortar reduced with an increase in MK replacement level. Among all the mixtures prepared, the binary blend with 3% NS exhibited the highest efficiency at all ages up to 56 days. The k-factors of NS3 were 2.29 and 2.02 at 28 and 56 days, respectively. This could be attributed to the higher pozzolanic activity of the NS particles, even at small replacement levels, which reacted with the CH to form a more structured and strength-carrying CSH gel.

In ternary blended mortars, all blends of MK10NS combinations showed a high efficiency of more than 1. Since the efficiency of ternary blends was influenced by the combined activity of MK and NS, the higher k-factor of MK10NS4.5 can be attributed to the consumption of more CH in the presence of highly reactive NS particles. A k-factor of 1.69 at 28 days in the ternary blend of MK10NS4.5 indicates a mass ‘M' of the MK10NS4.5 combination in the given proportion would be equivalent to a mass of 1.69M of cement in terms of strength development. Ternary blends comprising MK15 or MK20 with NS exhibited a k-factor lower than 1, except for the case of MK15NS4.5 at 3 and 7 days. Notably, an increase in MK content led to a reduction in k-factor, while an increase in NS content resulted in an increase in k-factor for the ternary blends.

Any k-factor higher than 1 indicates the higher cementing efficiency of pozzolan at that particular age in terms of compressive strength, while a k-factor less than 1 suggests that it is less efficient. The highest k-factors were observed in NS binary blends due to the development of high strength with their small replacement levels. It was also observed that the k-factor was the same (1.53) at 56 days when MK10 was combined with 3% and

4.5% NS. It can be concluded that the combination of 10% MK and 3% NS blends represents the most effective composition for developing compressive strength.

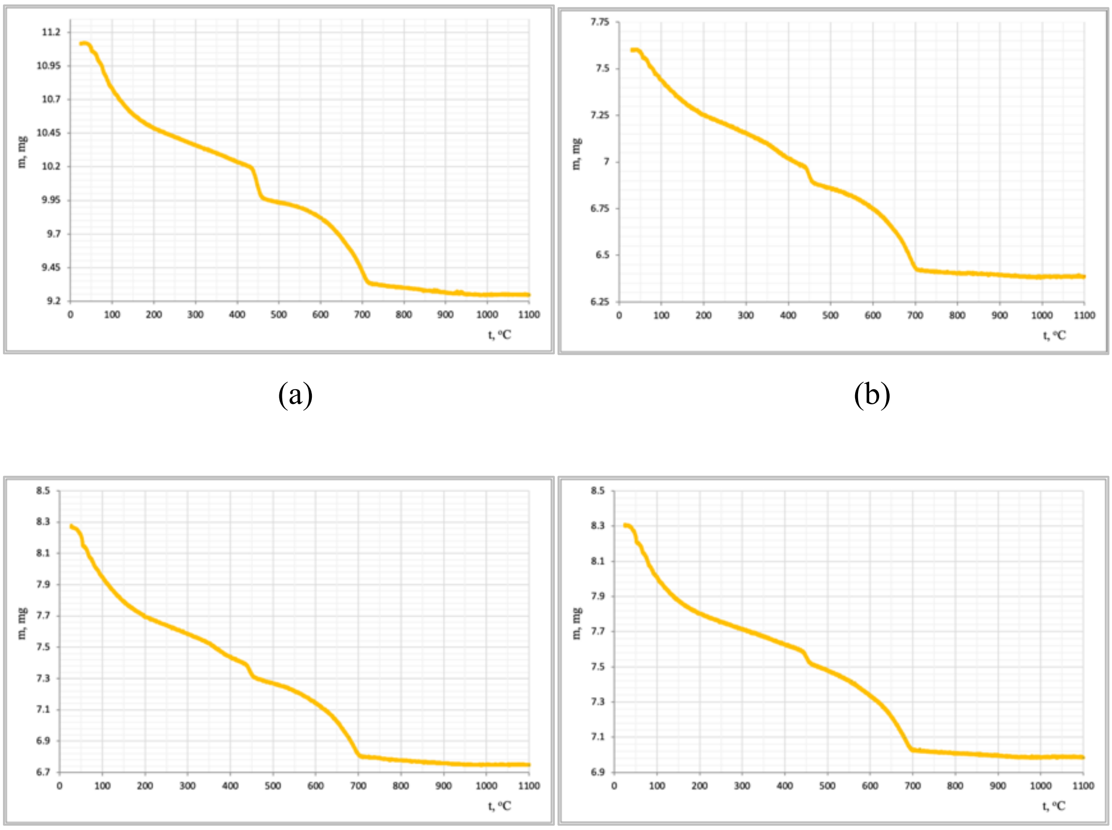
The relative strength value greater than 1 implies a higher k-factor, indicating that the pozzolan possesses superior cementing efficiency compared to the cement. Conversely, suppose the relative strength value is less than 1. In that case, the k-factor will also be less than 1, implying that the pozzolan or its combinations are less effective in contributing to strength compared to the cement.

The approach for determining the k-factor of blended cement mixtures has limitations due to factors such as mineral composition, curing conditions, age, cement type, strength grade, and pozzolan-to-cement ratio. Nevertheless, it provides increased assurance in the design of mixtures incorporating specific pozzolans at different levels with high efficiency in proportioning.

4.5 Characterisation techniques

4.5.1 Thermogravimetric analysis (TGA)

TG curves for CM, MK10, CNS4.5, and MK10NS4.5 mortar samples after 28 days of curing are shown in Figure 4.9. TG curve provides a visual representation of the weight changes of blended cement mortar as a function of temperature, ranging from ambient temperature to 1100° C. The typical pattern observed in the curve was a decrease in weight as the temperature increased due to the loss of water and other volatile components from the mortar.



(a) (b)

(c) (d)

Figure 4.9 TGA curve for a). reference (CM) b). MK10, c). NS4.5 and d). MK10NS4.5 mortar samples

The TGA weight loss (percentage) observed in the CM, MK10, NS4.5, and MK10NS4.5 mortar powders during the dehydration of hydration products occurs between 110-650°C, given in Table 4.1. The weight loss was observed to increase as the OPC content decreased, indicating more hydration products in blended mortars, with MK10NS4.5 forming more. The percentage weight loss of the samples obtained is consistent with the compressive strength results.

Table 4.1 Weight loss from TGA analysis

ID	%Weight loss*
CM	9.2
MK10	9.6
NS4.5	10.3
MK10NS4.5	10.7
*Weight loss in the range of 110-650°C	

4.5.2 X-ray diffraction (XRD) analysis

XRD patterns, as shown in Figure 4.10 of the various mortar compositions, revealed the presence of several crucial crystalline minerals of hydrated phases, including portlandite (CH), alite (C3S), and belite (C2S), as well as dicalcium aluminate (C2A), calcium carbonate ($CaCO_3$) and quartz. The XRD pattern was in line with TG analysis as the height of basic peaks of CH were lower for mortars MK10, NS4.5 and MK10NS4.5 due to pozzolanic activity of MK, NS and a combination of MK and NS [250–252].

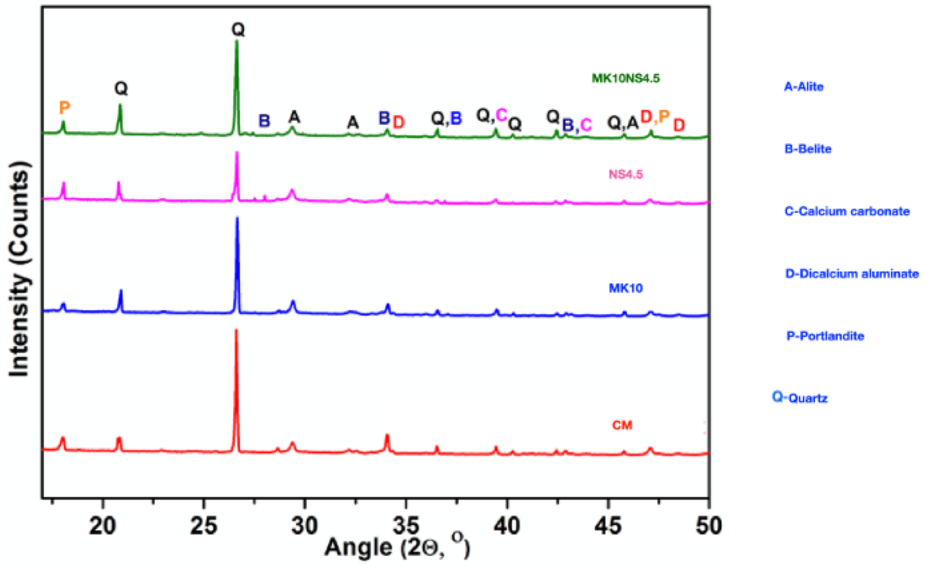


Figure 4.10 XRD patterns of CM, MK10, NS4.5 and MK10NS4.5 mortar powders

4.5.3 Morphology

Figure 4.11 (a-d) show the morphologies of the cement, MK10, NS4.5, and MK10NS4.5 paste compositions, respectively. The morphological analysis revealed differences in the formation of hydration products with micro-pores. As seen in Figure 4.11a the CM paste displayed the presence of ettringite (Ett) in the form of small needles and long CH crystals. Figure 4.11b shows that the MK10 hydrates had a texture composed of AFm, CH, and ettringite. The NS4.5 composition, as seen in Figure 4.11c demonstrated a more uniform and denser microstructure with the formation of ettringite and AFm phases. Figure 4.11d reveals that the MK10NS4.5 composition contained a significant amount of ettringite with small needle-like structures and CSH.

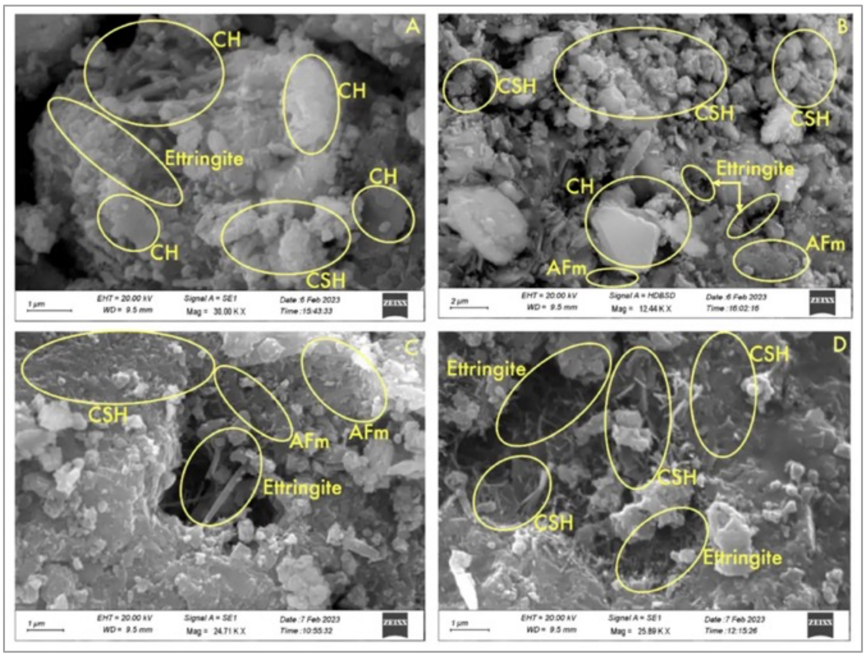
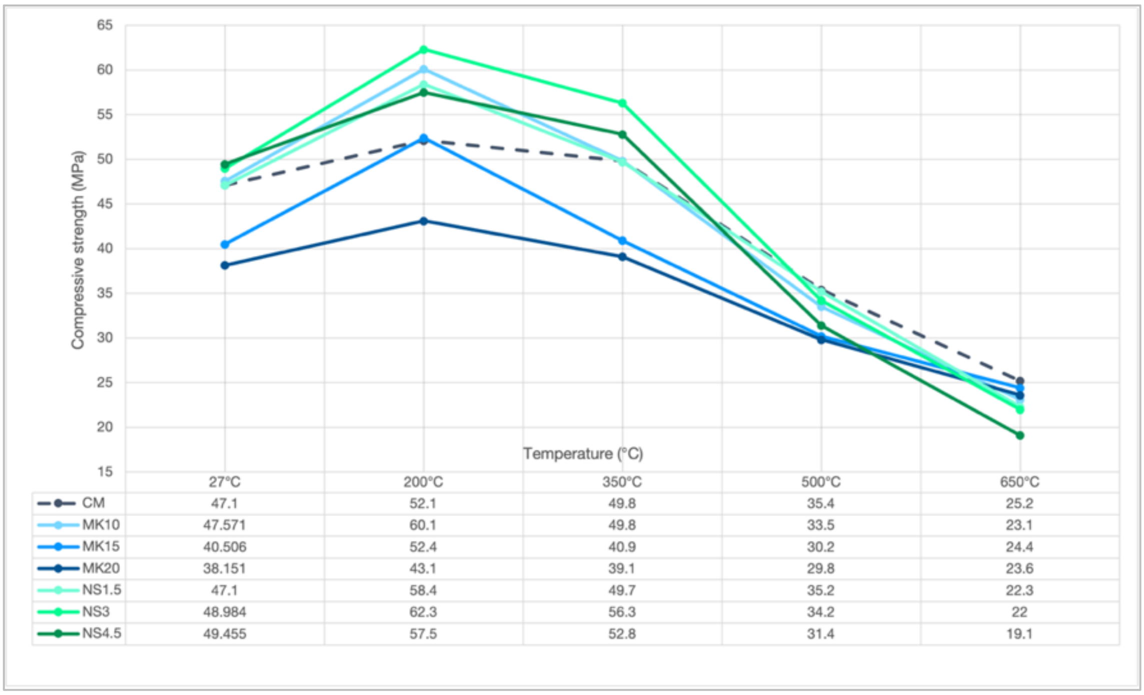


Figure 4.11 SEM images of a) reference cement paste, b) MK10 blended cement paste, c) NS4.5 blended cement paste, d) MK10NS4.5 blended cement paste

4.6 Thermal stability

4.6.1 Residual compressive strength

The compressive strength results of different mortar mixes at elevated temperatures revealed a consistent trend of strength gain at 200°C, followed by gradual strength loss at higher temperatures. Figure 4.12 and Figure 4.13 illustrate the temperature-dependent variations in compressive strength of CM, binary, and ternary blended cement mortars.



	27°C	200°C	350°C	500°C	650°C
CM	47.1	52.1	49.8	35.4	25.2
MK10	47.571	60.1	49.8	33.5	23.1
MK15	40.506	52.4	40.9	30.2	24.4
MK20	38.151	43.1	39.1	29.8	23.6
NS1.5	47.1	58.4	49.7	35.2	22.3
NS3	48.984	62.3	56.3	34.2	22
NS4.5	49.455	57.5	52.8	31.4	19.1

Figure 4.12 Compressive strength vs. temperature - CM with binary compositions, Abhilash et al. [234]

At a temperature of 27°C, the CM mortar exhibited a strength of 47.1 MPa, which rose to 52.1 MPa when subjected to a temperature of 200°C. Subsequently, the strength declined to 49.8 MPa at 350°C, further declining to 35.4 MPa at 500°C, and significantly dropped to 25.2 MPa at 650°C. On the other hand, when compared to the CM, binary blended mortars MK10 and MK15 displayed higher strengths at 200°C. At this temperature, the MK10 blend exhibited a strength of 60.1 MPa. However, as the temperature increased to 350°C, the strength decreased to 49.8 MPa, further declining to 33.5 MPa at 500°C and significantly dropping to 23.1 MPa at 650°C.

The MK15 blend also showed a similar trend, with strengths of 52.4 MPa at 200°C, 40.9 MPa at 350°C, 30.2 MPa at 500°C, and 24.4 MPa at 650°C, slightly higher than the MK10 blend at 650°C. On the other hand, the MK20 blend mortar exhibited a strength of 43.1 MPa at 200°C, which reduced to 39.1 MPa at 350°C, 29.8 MPa at 500°C, and 23.6 MPa at 650°C. Notably, the MK20 blend had lower strength than the MK10 and MK15 blends at all elevated temperatures, except at 650°C, where it showed slightly higher strength than MK10. This observation could be attributed to the agglomeration of fine MK particles around the OPC grains, impeding the hydration process.

A continuous decrease in compressive strength in MK concrete with an increase in temperature was reported by Nadeem et al. [161]. It is interesting to note that MK10 had the highest strength gain at 200°C compared to the other binary blends, indicating its potential as a pozzolanic material to enhance the strength of mortar at elevated temperatures. Bu et al. [253] reported that the inclusion of MK resulted in significantly increased strength at or above 150°C, which was attributed to forming a dense microstructure with minimal porosity due to MK's filler effect. However, at 650°C, MK10 also had the highest strength reduction among all mortar compositions, suggesting that the dehydration of hydrates, which released free moisture and left behind a reduced amount of water content, might contribute to the formation of micro-cracks, ultimately leading to a decrease in strength. A denser structure exposed to higher temperatures is more susceptible to this phenomenon [254]. Poon et al. [158] reported enhanced vapour pressure at elevated temperatures in the dense pore structure of the MK concrete. High vapour pressure formed within the denser structure of mortar or concrete can cause the formation of microcracks within the structure, potentially affecting its overall strength [255–257].

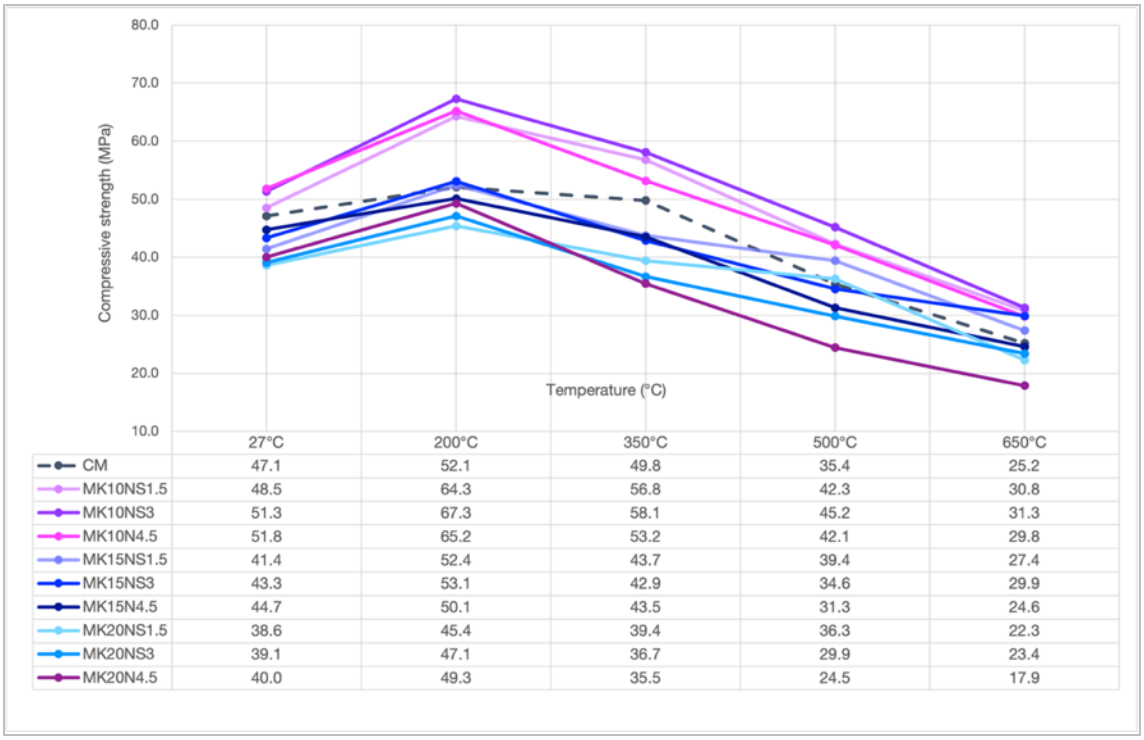
Additionally, high temperatures can cause the thermal decomposition of the cementitious materials and the pozzolanic additives, decreasing the mortar's overall strength [258]. Agglomeration of fine particles, as observed in the MK20 blend, can also lead to reduced strength due to hindered hydration and decreased bonding between particles.

NS binary blended mortars exhibited comparable and superior performance at elevated temperatures compared to MK binary blended mortars. Previous research also highlighted the thermal stability of concrete incorporating NS [259,260]. Compared to CM, the strength of NS binary blended mortars increased substantially at 200°C, with NS3 exhibiting the highest strength at 62.3 MPa, followed by NS1.5 at 58.4 MPa and NS4.5 at 57.5 MPa. This increase in strength can be ascribed to the high pozzolanic reaction of NS with a high surface area, which facilitated the formation of additional CSH and decreased porosity, thereby enhancing the strength.

However, as the temperature rose to 350°C, 500°C, and 650°C, the strength declined for all mixes. NS1.5 showed the highest strength at 650°C with 22.3 MPa, followed by NS3 at 22.0 MPa and NS4.5 at 19.1 MPa, the lowest among all MK and NS binary blends. The decrease in strength at high NS dosage may be ascribed to the deterioration of NS at high temperatures, which may lead to the loss of its pozzolanic activity and reduce the overall bonding and strength of mortar mixes. Similar findings were also reported by Horszczaruk et al. [261], who observed that 3% NS improved the thermal resistance of cement mortar up to 200°C, but the effect was not significant at higher temperatures, consistent with the results of this study. Abd. El. Aleem et al. [262] observed that the thermal expansion of concrete incorporated with NS resulted from the continued hydration of cement phases and the pozzolanic reaction of NS. According to Heikal et al. [260], the interaction between the NS and the cementitious matrix at elevated temperatures can affect the performance of binary composites containing NS.

Like the binary blended mortars, the strength of the ternary blends of MK and NS increased as the temperature rose to 200°C before declining as the temperature rose higher. However, the specific trends and magnitudes of strength changes differ depending on the composition of the mortar mix. Compared with binary blends of MK and NS, ternary blended mortars of MK10 and MK15 compositions exhibited comparable or higher strengths at elevated temperatures. This can be due to the higher CH consumption in OPC-MK-NS blends at elevated temperatures [260].

At a temperature of 200°C, ternary blended mortars exhibited greater strength when compared to corresponding binary blends of MK and NS. MK10NS1.5, MK10NS3, and MK10NS4.5 showed strengths of 64.3 MPa, 67.3 MPa, and 65.2 MPa, respectively. Strengths of MK15NS1.5, MK15NS3, and MK15NS4.5 were 52.4 MPa, 53.1 MPa, and 50.1 MPa, respectively. Finally, MK20NS1.5, MK20NS3, and MK20NS4.5 had strengths of 45.4 MPa, 47.1 MPa, and 49.3 MPa, respectively. This suggests that adding MK and NS can potentially improve the strength of the mortar at lower temperatures.



	27°C	200°C	350°C	500°C	650°C
CM	47.1	52.1	49.8	35.4	25.2
MK10NS1.5	48.5	64.3	56.8	42.3	30.8
MK10NS3	51.3	67.3	58.1	45.2	31.3
MK10N4.5	51.8	65.2	53.2	42.1	29.8
MK15NS1.5	41.4	52.4	43.7	39.4	27.4
MK15NS3	43.3	53.1	42.9	34.6	29.9
MK15N4.5	44.7	50.1	43.5	31.3	24.6
MK20NS1.5	38.6	45.4	39.4	36.3	22.3
MK20NS3	39.1	47.1	36.7	29.9	23.4
MK20N4.5	40.0	49.3	35.5	24.5	17.9

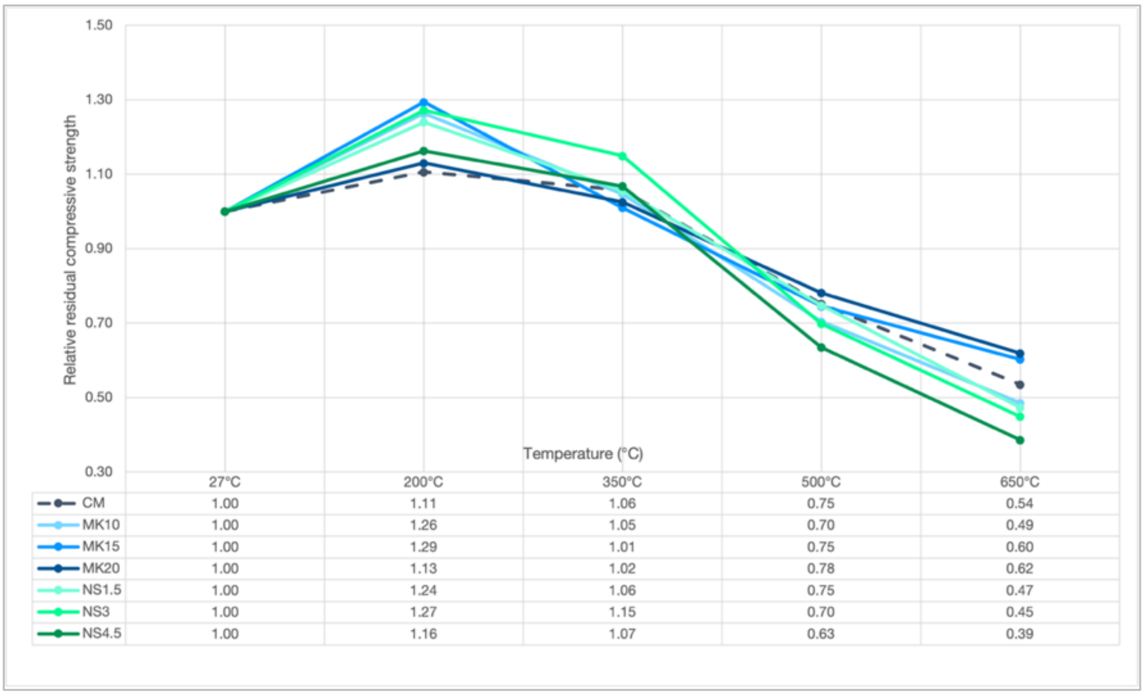
Figure 4.13 Compressive strength vs. temperature - CM with ternary compositions, Abhilash et al. [234]

As the temperature progressively increased to 350°C, 500°C, and 650°C, the strength of ternary blended mortars experienced a noticeable decline compared to the binary blends. Specifically, at 350°C, MK10NS1.5 exhibited a strength of 56.8 MPa, while MK10NS3 and MK10NS4.5 achieved strengths of 58.1 MPa and 53.2 MPa, respectively. As the temperature rose to 500°C, the strength of MK10NS1.5 decreased to 42.3 MPa, while MK10NS3 and MK10NS4.5 reached strengths of 45.2 MPa and 42.1 MPa, respectively. Finally, at 650°C, MK10NS1.5, MK10NS3, and MK10NS4.5 demonstrated strengths of 30.8 MPa, 31.3 MPa, and 29.8 MPa, respectively. Comparable patterns were also observed in the MK15NS and MK20NS compositions.

After comparing various mortar compositions, it was evident that MK10NS3 consistently exhibited higher strengths across all temperatures. Colloidal NS in cement accelerated the hydration process by transforming the less rigid CSH into a denser and more rigid CSH gel, as explained by Pengkun Hou et al. [194]. Additionally, incorporating up to 3% NS could have led to a significant reduction in CH levels due to the pozzolanic reaction, resulting in improved strength, enhanced concrete density, and microstructure refinement, according to Said et al. [263]. However, at 650°C, although MK10NS3 demonstrated higher strength than other ternary blended mortars of MK10NS and MK15NS, the difference in strength was relatively smaller.

4.6.2 Thermal resistance

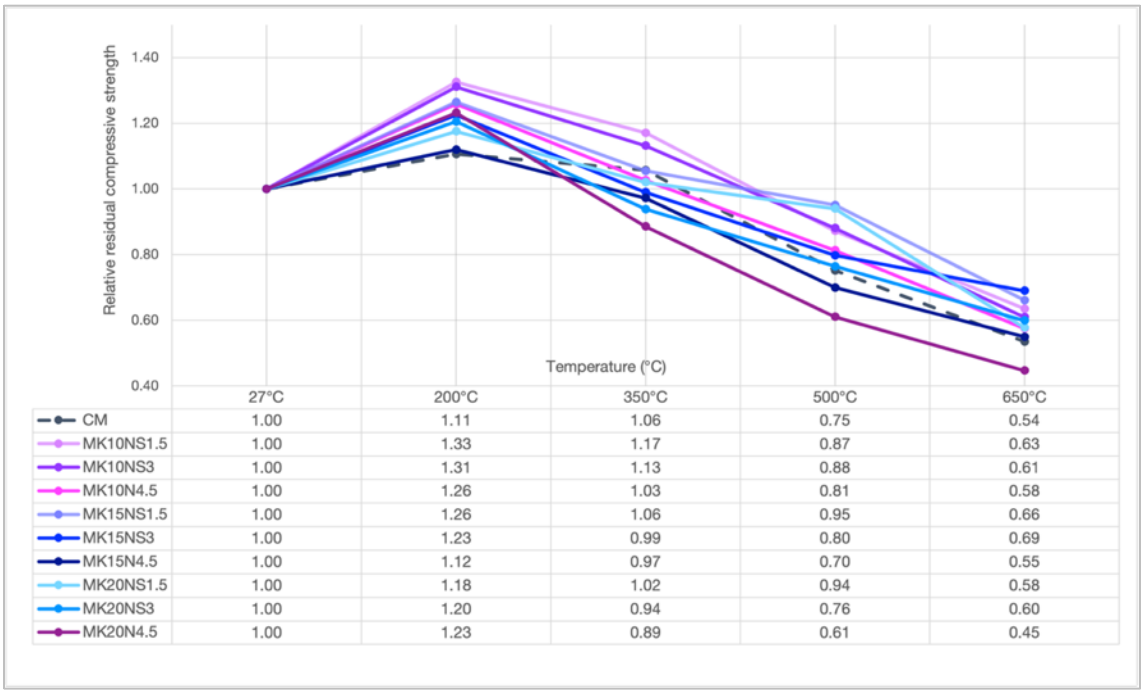
The thermal or heat resistance of different mortars can be evaluated by comparing the areas under the relative residual compressive strength curve, as proposed by Abdelmelek and Lubloy [79].



	27°C	200°C	350°C	500°C	650°C
CM	1.00	1.11	1.06	0.75	0.54
MK10	1.00	1.26	1.05	0.70	0.49
MK15	1.00	1.29	1.01	0.75	0.60
MK20	1.00	1.13	1.02	0.78	0.62
NS1.5	1.00	1.24	1.06	0.75	0.47
NS3	1.00	1.27	1.15	0.70	0.45
NS4.5	1.00	1.16	1.07	0.63	0.39

Figure 4.14 Relative residual compressive strength vs. temperature for binary compositions

The relative residual compressive strength was determined by comparing the compressive strength of mortars at different temperature levels with the compressive strength of the same mortar before heating (at room temperature of 27±2°C). Resulting ratios were plotted for binary (Figure 4.14) and ternary blends (Figure 4.15). The curve areas provided (in Figure 4.16) insight into the performance of each mortar under elevated temperatures.



	27°C	200°C	350°C	500°C	650°C
CM	1.00	1.11	1.06	0.75	0.54
MK10NS1.5	1.00	1.33	1.17	0.87	0.63
MK10NS3	1.00	1.31	1.13	0.88	0.61
MK10N4.5	1.00	1.26	1.03	0.81	0.58
MK15NS1.5	1.00	1.26	1.06	0.95	0.66
MK15NS3	1.00	1.23	0.99	0.80	0.69
MK15N4.5	1.00	1.12	0.97	0.70	0.55
MK20NS1.5	1.00	1.18	1.02	0.94	0.58
MK20NS3	1.00	1.20	0.94	0.76	0.60
MK20N4.5	1.00	1.23	0.89	0.61	0.45

Figure 4.15 Relative residual compressive strength vs. temperature for ternary compositions

Among tested mortars, the highest area under the curve was observed for MK10NS1.5, with a value of 405.38, indicating a slightly higher heat resistance than the MK10NS3. This result suggests that combining 10% MK and 1.5% NS components enhanced mortars' ability to withstand high temperatures and retain their compressive strength. In other words, when exposed to elevated temperatures, the MK10NS1.5 mortars experienced less reduction in strength from their initial strength. Mortar MK10NS3 and MK10NS4.5 also exhibited notable areas under the curve, measuring 396.55 and 359.95, respectively, indicating their significant heat resistance capabilities. MK15NS1.5 and NS1.5 displayed comparable performance, with curve areas of 391.93 and 343.44, respectively, suggesting their effectiveness in maintaining strength under elevated temperatures. On the other hand, mortars with lower curve areas, such as MK20NS4.5 (294.16), MK15NS4.5 (310.12), and NS4.5 (309.42), suggest relatively lower heat resistance compared to the previously mentioned mortars. These results indicate that a higher dosage of MK and NS may lead to a decrease in heat resistance.

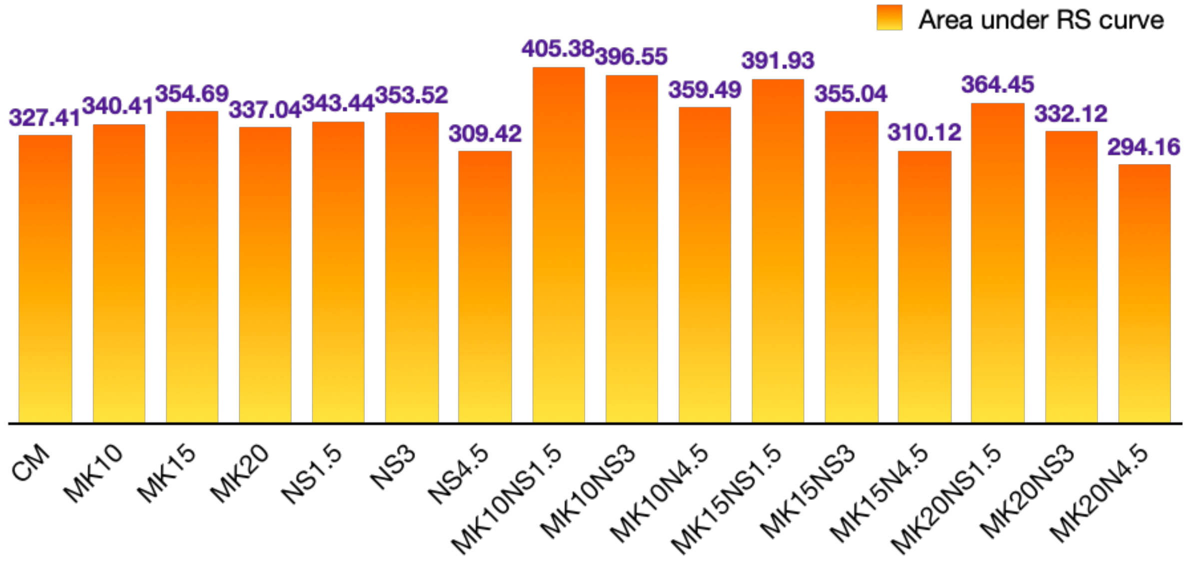


Figure 4.16 Heat resistance as the area under the curve of the relative strength of the mortar compositions Abhilash et al. [234]

4.6.3 Surface cracking, spalling and spalling frequency

Hardened blended cement mortars underwent chemical and physical changes at elevated temperatures according to their exposed temperature level. The formation of cracks in the mortars depends on the internal vapour pressure caused by the moisture within the pores of mortars or on thermal expansion. Ichikawa and England [264] reported that the pore pressure increased as the temperature increased. Pores in concrete can act as pathways [256] for steam to escape during heating, thereby reducing the internal vapour pressure and the potential for cracking. Therefore, when the pore structure is refined or densified, it becomes more difficult for steam to escape, leading to higher internal vapour pressures and an increased risk of cracking and spalling. The spalling shows the thermal instability of the samples.

When considering the pore structure of mortar or concrete, a more porous and open configuration can facilitate the release of steam when subjected to heat. As a result, this helps to decrease the internal vapour pressure and minimise the risk of cracking. The presence of pores in the material functions akin to pressure relief valves, enabling the steam to escape without accumulating excessive internal pressure. On the other hand, if the concrete matrix possesses refined pore structures, it can impede the free movement of steam, potentially leading to the development of high internal pressure. Consequently, the refined structure of the pores within the mortar matrix may contribute to forming cracks in mortars containing MK when exposed to elevated temperatures.

Surface cracks on sixteen combinations of mortars including the reference mortar exposed to elevated temperatures of 500°C and 650°C are shown in Figure 4.17.

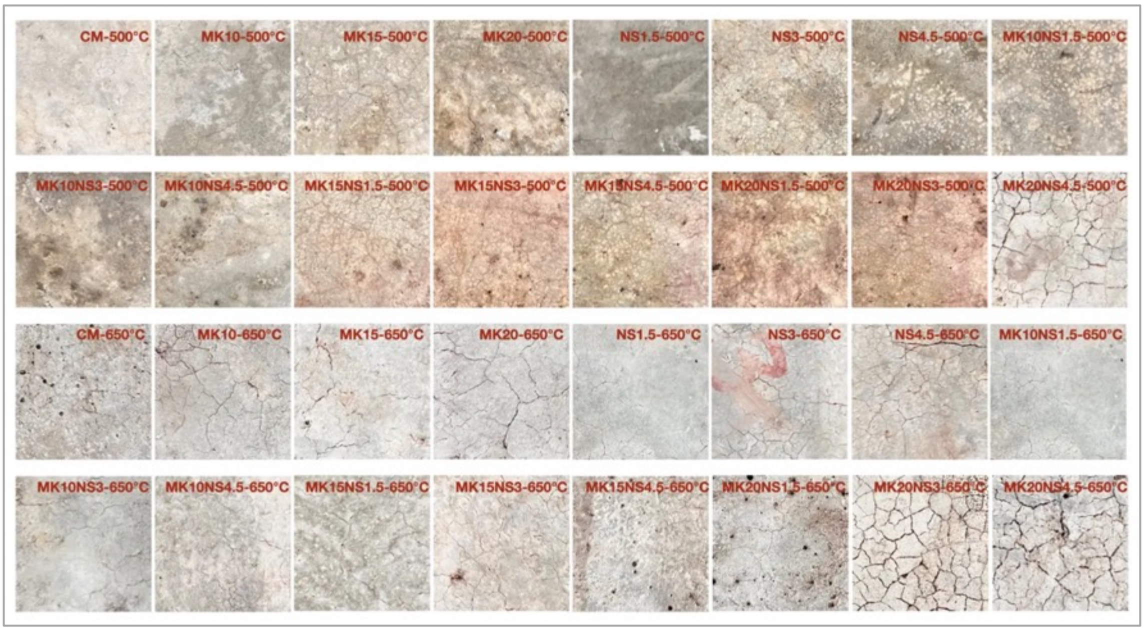


Figure 4.17 Surface cracks on mortars exposed to elevated temperatures of 500°C and 650°C

No cracks were observed on the surface of the mortar treated up to 350°C. However, when subjected to a temperature above 350°C, almost all mortar samples developed cracks on the surface, and some samples also had pitting on the surface. Large cracks were observed on mortars treated at 650°C. It was observed that the mortar specimen suffered spalling and appeared to have fewer cracks on the surface. Therefore, it can be inferred that the internal vapour pressure created by steam at high temperatures resulted in the explosion of the sample. Spalling can occur through two distinct mechanisms [158]. The first mechanism involves the build-up of vapour pressure caused by the dense cement paste, which restricts moisture escape and leads to increased pressure, ultimately causing spalling. The second mechanism relates to thermal stress, wherein the heat from fire exposure creates a temperature gradient within the concrete, generating internal stresses and spalling. These mechanisms can also coexist, potentially exacerbating the spalling phenomenon. The spalled mortar cubes of MK10, NS3 and MK10NS3 are shown in Figure 4.18

Figure 4.18 Spalled mortar cubes (MK10, NS3, MK10NS3)

High pore pressures play a significant role in causing concrete spalling [265,266]. Spalling occurs when the internal vapour pressure and thermal strain exceed the tensile strength of the concrete. However, Spalling cannot be exclusively attributable to the increase in internal pressure. When a crack formed by pore pressure starts to open or widen, the inner pore pressure quickly decreases. This shows that spalling was only triggered by pore pressure. Thermal compressive stresses are necessary for the crack's expansion and the subsequent explosive spalling. Consequently, it is still difficult to comprehend this complicated phenomenon [267,268]. The splitting crack, as shown in Figure 4.18 may be attributed to the thermal compressive stress, which is parallel to the heated surface, as reported by [268].

Figure 4.19 illustrates the frequency of spalling in different mortars, where the material's surface breaks off. Spalling frequency refers to the percentage of samples that experienced spalling when exposed to temperatures up to 650°C, compared to the total number of samples tested. The findings indicate that spalling predominantly occurred in mortars containing MK. This can be attributed to the compact pore structure present in MK-based mortars, which traps vapour and leads to explosive spalling. Specifically, the mortar incorporating 10% MK and 3% NS exhibited a high spalling frequency. Mortars spalled at 650°C except for the MK10NS3 mortars, which spalled at 500 and 650°C.

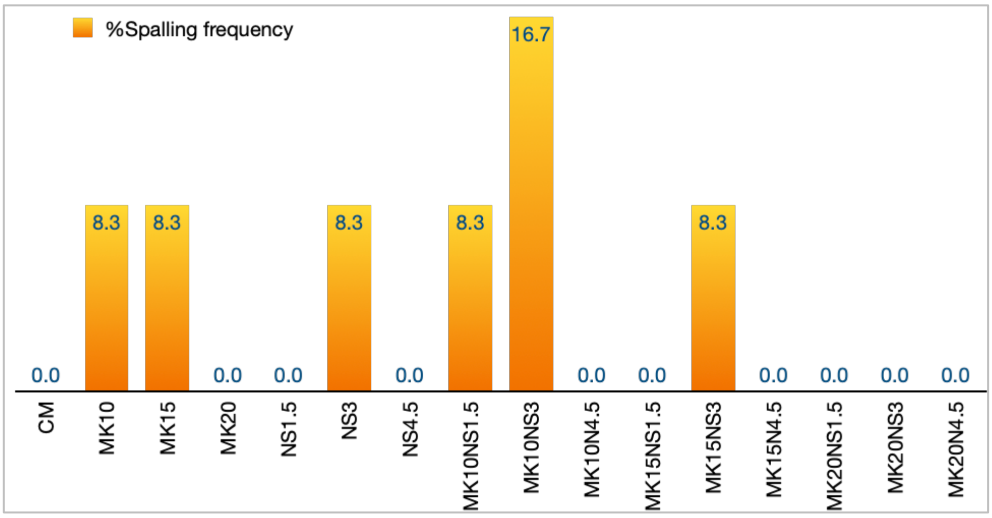


Figure 4.19 Spalling frequency of mortars, Abhilash et al. [234]

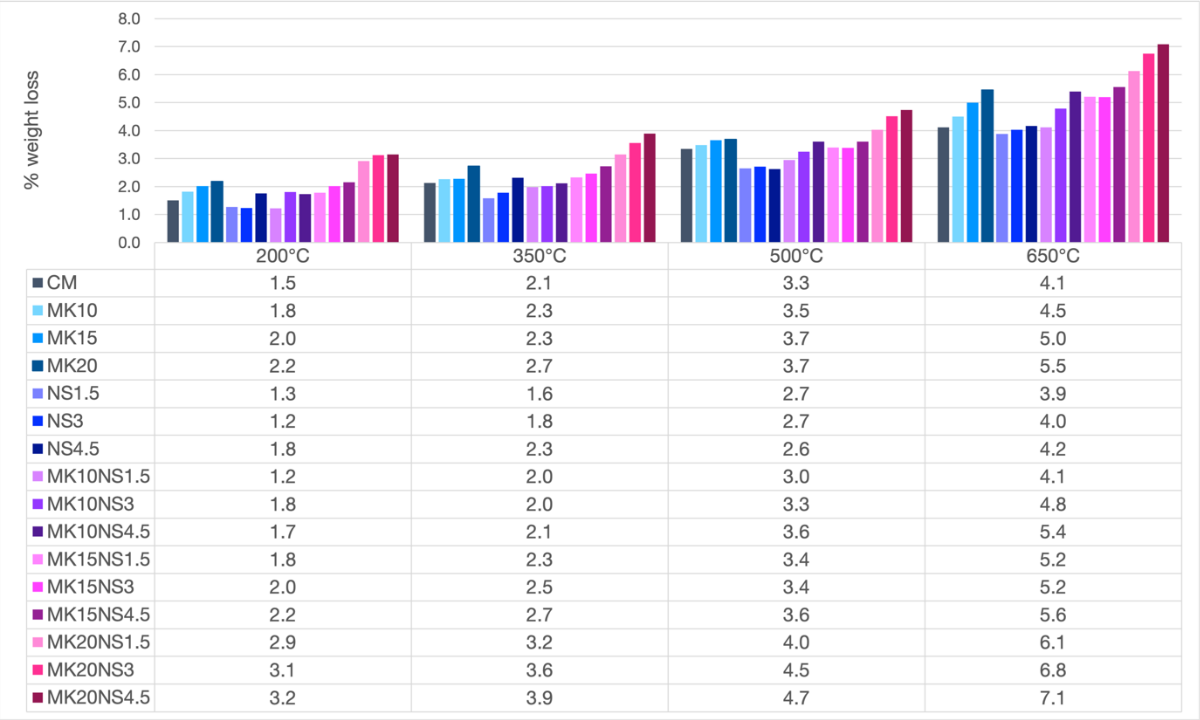
4.6.4 Weight loss

Cement-based composites tend to lose weight when exposed to high temperatures, typically due to the evaporation of water in the concrete. To measure the extent of weight loss, the weight of the mortar specimens before and after the heat treatment were compared. The percentage weight loss was calculated using Equation 1. The weight loss was observed to increase with increasing both MK and NS. The ternary composition of MK20 had the highest weight loss.

$$\text{Weight loss} = \frac{W_1 - W_2}{W_1} \ x\ 100 \qquad \text{Equation 4.1}$$

W_1 is the initial weight (g) of the mortar specimen, and W_2 is the weight (g) of the mortar specimen after exposure to the elevated temperature. The weight loss was maximum at 650°C. The high temperatures can cause the water in the mortar to evaporate, leading to weight loss. As the water evaporates, it may also leave voids in mortars, thus weakening their structure.

Figure 4.20 illustrates the percentage weight loss of different mortar compositions at varying temperatures. It was observed that increasing the temperature leads to higher weight loss in the mortar samples. Moreover, the replacement levels of MK and NS had a notable influence on weight loss, with higher replacement levels resulting in increased weight loss.



	200°C	350°C	500°C	650°C
■ CM	1.5	2.1	3.3	4.1
■ MK10	1.8	2.3	3.5	4.5
■ MK15	2.0	2.3	3.7	5.0
■ MK20	2.2	2.7	3.7	5.5
■ NS1.5	1.3	1.6	2.7	3.9
■ NS3	1.2	1.8	2.7	4.0
■ NS4.5	1.8	2.3	2.6	4.2
■ MK10NS1.5	1.2	2.0	3.0	4.1
■ MK10NS3	1.8	2.0	3.3	4.8
■ MK10NS4.5	1.7	2.1	3.6	5.4
■ MK15NS1.5	1.8	2.3	3.4	5.2
■ MK15NS3	2.0	2.5	3.4	5.2
■ MK15NS4.5	2.2	2.7	3.6	5.6
■ MK20NS1.5	2.9	3.2	4.0	6.1
■ MK20NS3	3.1	3.6	4.5	6.8
■ MK20NS4.5	3.2	3.9	4.7	7.1

Figure 4.20 Percentage weight loss of mortars vs. temperature Abhilash et al. [234]

The CM experienced weight loss of 1.5% at 200°C and 4.1% at 650°C. Comparing the binary blends of MK10, MK15, and MK20 mortars at 200°C, it is evident that MK10 had the lowest weight loss of 1.8%, followed by MK15 at 2.0% and MK20 at 2.2%. However, as the temperature rose to 650°C, binary blends of MK mortars exhibited higher weight loss ranging from 4.5% to 5.5%. The weight loss of the binary blends of NS1.5, NS3, and NS4.5 mortars at 200°C was observed to be 1.3%, 1.2%, and 1.8%, respectively and at 650°C the weight loss increased to 3.9%, 4.0%, and 4.2%. These results indicate that increasing the replacement level of MK and NS resulted in higher weight loss.

Furthermore, ternary blends of MK10 and NS at varying concentrations of 1.5, 3, and 4.5% exhibited weight loss of 1.2%, 1.8%, and 1.7%, respectively, at 200°C. At 650°C, the weight loss increased to 4.1%, 4.8%, and 5.4%, respectively. These results indicate that the ternary blends generally displayed higher weight loss than their binary counterparts. For CM, MK10, NS4.5, and MK10NS4.5, the order of mass loss from TG values at 28 days is comparable to the weight loss sequence in the same compositions at elevated temperatures.

Ternary mixes of MK15 and MK20 with NS had higher mass loss as summarised in Figure 4.20. The weight loss increased as the MK and NS replacement levels increased. At 200°C, MK15NS4.5 and MK20NS4.5 exhibited weight loss of 2.2 and 3.2%, respectively, and at 650°C, their weight loss was 5.6 and 7.1%, respectively.

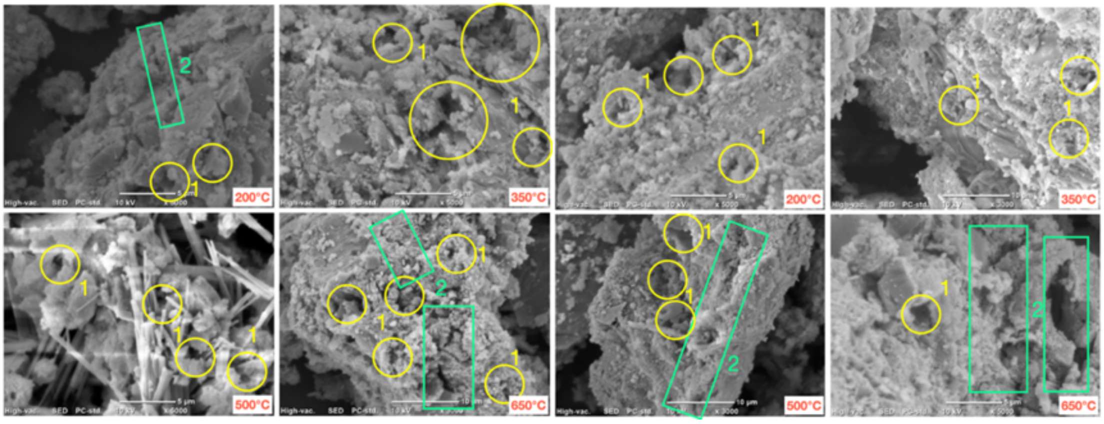
The initial weight loss observed in the mortar cubes can be attributed to the evaporation of capillary water, which dissipates rapidly. The loss of adsorbed and interlayer water also contributes to the overall weight reduction. Except for the CM, the degree of weight loss became increasingly pronounced as the temperature rose from 500°C to 650°C. According to Rashad and Sadek [269], weight loss above 400°C was primarily caused by the release of chemically bound water, which is part of the hydration products and is challenging to evaporate at lower temperatures. Therefore, weight loss beyond 400°C can be attributed to the release of chemically bound water. According to Nayel et al. [270] and Tantawy [273], the partial dehydration of CSH and the evaporation of gel pore water and macro capillary pore water may be responsible for weight loss at 300°C.

4.6.5 SEM analysis

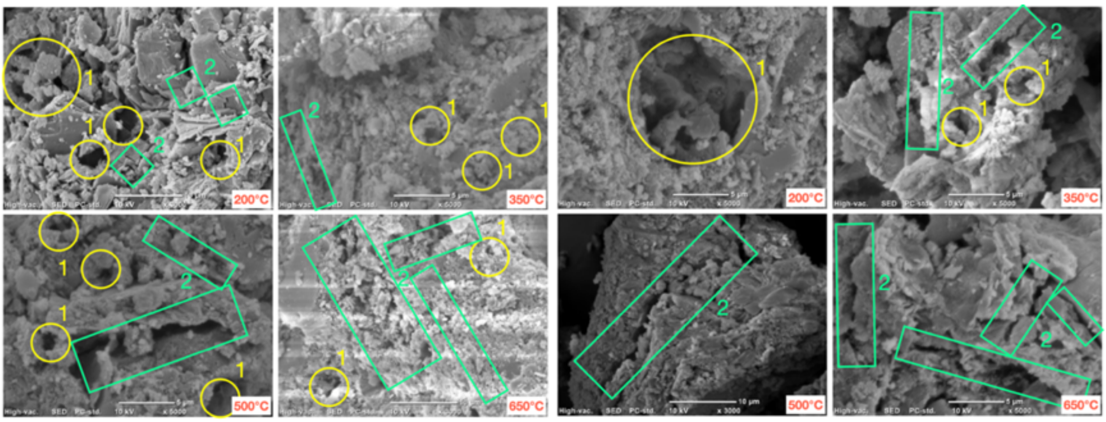
The hydration and dehydration of cement blend with MK and NS, exposed to elevated temperatures, resulted in microstructural changes and changes in phase compositions, as observed in SEM micrographs. Furthermore, the SEM micrographs also explain the morphological transformations in mortars caused by exposure to elevated temperatures. Up to a temperature of 650°C, the dominant CSH phase with layers of flakes was observed in all mortars. Microcracks and voids were also identified in the heated specimens' fragments, and their width and size increased with temperature. As a result, the microstructure became highly porous at 650°C, possibly due to the disintegration of CH above 350°C.

The SEM images, Figure 4.21*,* showed hydrated phases in a moderate grey colour, which decreased with increasing temperature. At 650°C, a significant change in the microstructure was observed, characterised by microcracks, voids, and decomposed CSH. Consequently, the compressive strength of mortars decreased. Mortars with MK and NS incorporation exhibited higher cracks and voids than those in the CM mortar, indicating an increase in the number and widening of microcracks in mortars with a denser microstructure. SEM images revealed the denseness in the microstructure of mortars with

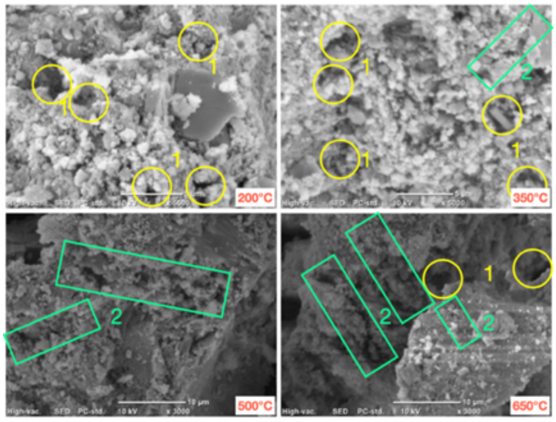
MK and NS, which is attributed to their presence. However, an increase in the MK replacement level led to a higher pore volume, possibly due to the agglomeration of fine MK particles at higher replacement levels, hindering their uniform dispersion in the mixture. A similar scenario was observed in NS blended mortars, where the filler effect of NS reduced the pores and facilitated the additional formation of CSH gel, enhancing the bonding between fine aggregate particles.



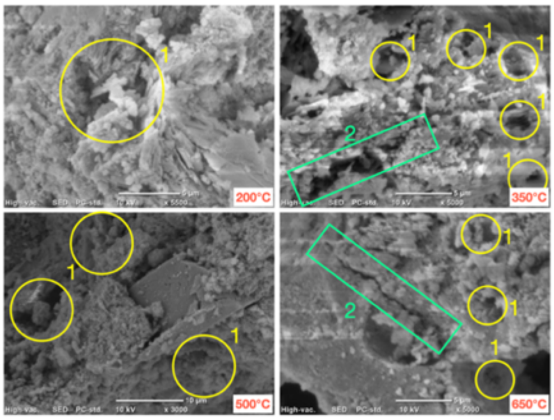
(a) CM (b) MK10



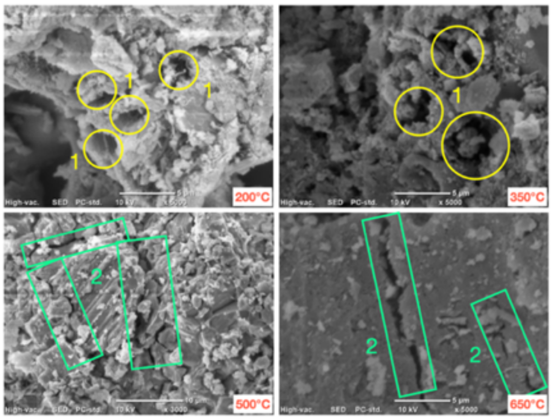
(c) MK15 (d) MK20



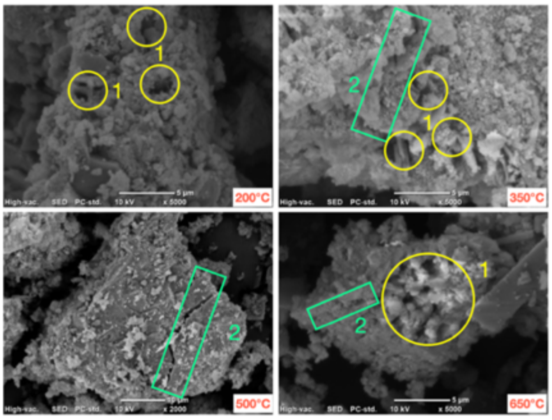
(e) NS1.5



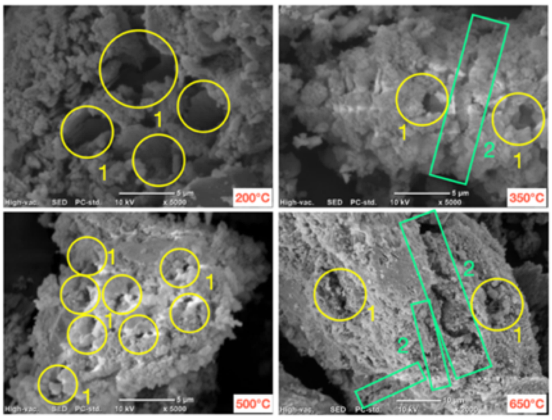
(f) NS3



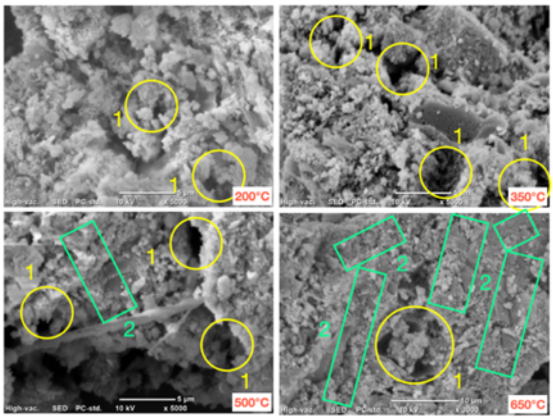
(g) NS4.5



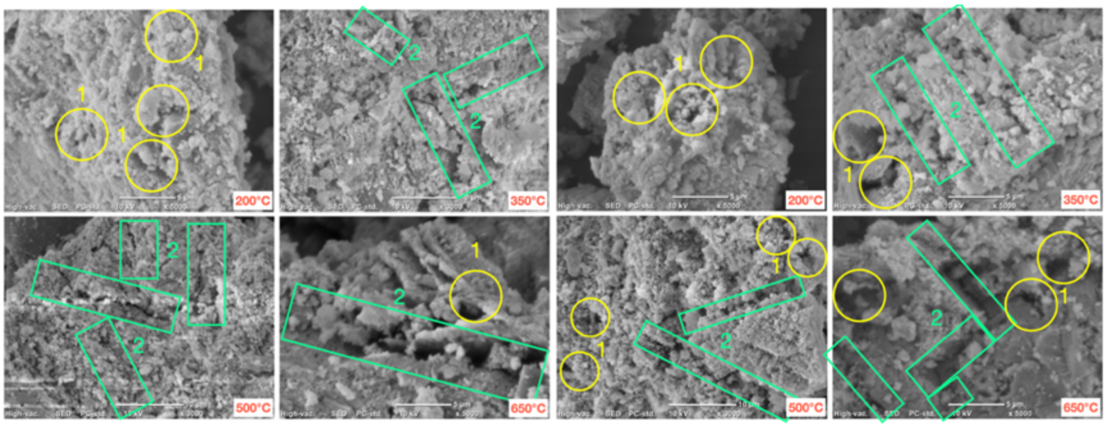
(h) MK10NS1.5



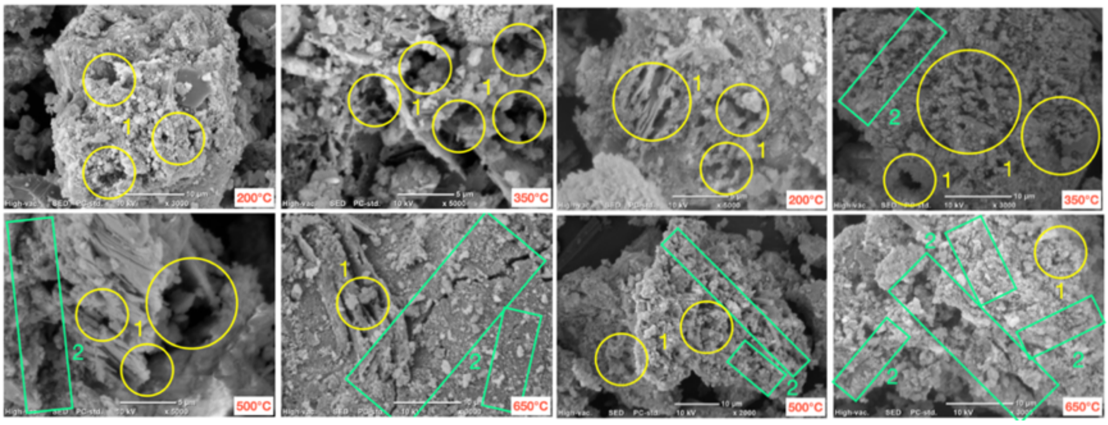
(i) MK10NS3



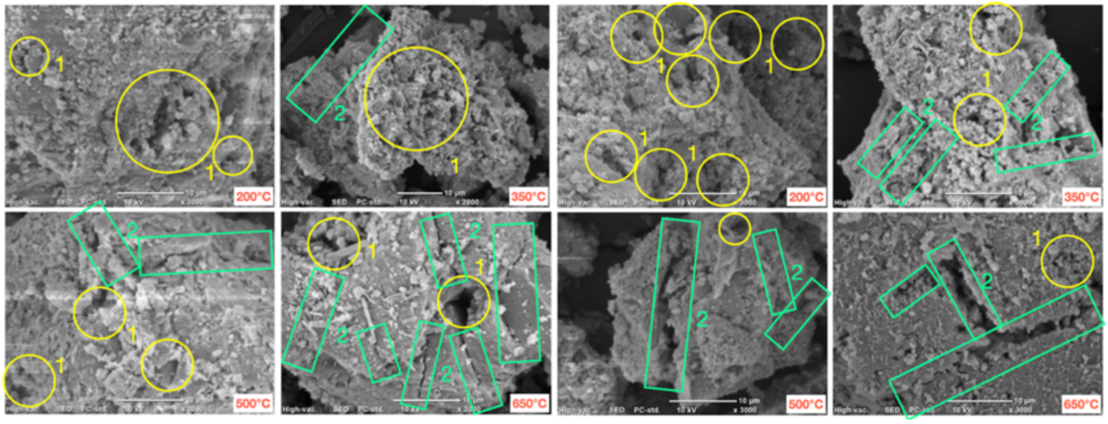
(j) MK10NS4.5



(k) MK15NS1.5 (l) MK15NS3



(m) MK15NS4.5 (n) MK20NS1.5



(o) MK20NS3 (p) MK20NS4.5

Figure 4.21 SEM images of mortars treated at 200, 350, 500 and 650°C (Circles represent voids and boxes represent cracks)

4.7 Summary

The study revealed that a 10% replacement of OPC by MK led to the highest compressive strength in mortar, while higher MK dosages (15% and 20%) resulted in decreased strength due to insufficient cement hydration for a pozzolanic reaction on MK particles' surfaces. Compressive strength increased with higher NS dosages up to 4.5%, attributed to both pozzolanic reactions and the influence of nanoparticles on the CSH gel structure. However, limited strength increase at higher NS dosages was observed due to uneven distribution and agglomeration during manual preparation. Adding MK and NS improved compressive strength, with the ternary blend MK10NS3 demonstrating the highest strength. Thermal resistance evaluation highlighted MK10NS1.5 as having the highest resistance, emphasising its ability to withstand high temperatures while preserving compressive strength. However, higher MK and NS dosages reduced thermal resistance, leading to visible cracks and spalling at elevated temperatures, particularly notable in the MK10NS3 composition.