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Mechanical, Durability and Microstructure Analysis Overview of Concrete Made with Metakaolin (MTK)

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Abstract: Metakaolin (MTK) has received a lot of interest in the past two decades as a supplemental cementitious ingredient. MTK is actively being utilized in concrete and there is a large body of literature on the characteristics of concrete containing MTK. A rigorous evaluation of the use of MTK in concrete, however, is lacking, which is required to better know its (MTK) benefits, mechanisms, past and current progress. As a result, the objective of this study is to deliver an overview of MTK utilized in concrete. The physical and chemical characteristics of MTK, as well as the hydration, workability, mechanical qualities, hydration durability, and microstructure analysis of MTK-based concrete, are discussed. A comparison of the findings of diverse literature is presented, as well as some key recommendations. The findings suggest that adding MTK to concrete enhances certain characteristics, particularly mechanical capabilities, but decreases concrete flowability. Improvement in the durability of concrete with MTK was also observed but, for this, less information is available. For optimal performance, the right dosage is crucial. The typical ideal range is between 10 to 20% by weight of the binder. Further research gaps into the characteristics of concrete containing MTK are also recommended.

Keywords: metakaolin; supplementary cementitious materials; sustainable concrete; mechanical and durability

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1. Introduction

Concrete production and usage in the building business have recently increased due to its dependability in terms of strength, durability, and economic characteristics when compared to other construction materials [1–5]. Globally, about one ton of concrete is produced yearly by each human [6].

The manufacturing of Portland cement, which is the primary ingredient in concrete, has a number of drawbacks, including significant energy consumption and pollution [7,8]. It is well known that the chemical process of calcination results in the release of a large quantity of carbon dioxide CO_2 both indirectly and directly due to the heating of limestone and the burning of fossil fuels to manufacture cement [7,9–11].

Cement is one of the most important ingredients in concrete since it uses water to bond fine and coarse particles. Cement production was over 4111.1 million tons per year in 2018 and this demand is continually increasing, releasing massive volumes of CO_2 into the environment and contributing to global warming [12]. As a result, the necessity to discover an alternate supply of cement is a major worry in today's society.

As a result, optimizing cement output and consumption is critical. The use of supplemental cementitious materials (SCMs) such as fly ash [13,14], silica fume [15], waste glass [16], waste marble [17], waste oil [18] and ground granulated blast furnace slag [19] is one solution to this problem while manufacturing concrete or as a partial substitute for cement in the cement industry. Higher ultimate strength, better durability, avoidance of excessive surface cracking of concrete in certain situations, economic benefits, and enhanced sustainability are all advantages of using most of the extra cementitious ingredients in concrete. The quantity of Portland cement replaced by secondary Cementitious material is determined by their pozzolanic activity [20]. A study also claims that coloured ultra-thin functional overlays contribute to infrastructure sustainability [21]. Several researchers have shown that MTK may be used as a cementitious ingredient in concrete [22–24].

The use of high reactivity MTK as a supplemental cementitious ingredient in the concrete industry has gained popularity. Although metakaolin has been known since the 1960s, researchers are still interested in its use as a pozzolanic ingredient in cement or as a cementitious material in concrete to further improve its performance [25,26]. MTK is an ultrafine pozzolana made by calcining purified kaolinite clay at temperatures between 700 and 900 °C to remove chemically bonded water and disrupt the crystalline structure [27]. Figure 1 shows the production process of MTK.

Figure 1. The production process of MTK [28].

Because of its higher level of purity, pozzolanic reactivity, and finer grading, the use of MTK is known to significantly refine the pore structure and reduce the calcium hydroxide of the cement matrix (hardened state) of the concrete. This is achieved as a result of the finer grading of the MTK. The reaction of MTK with $Ca(OH)_2$, which is produced during the hydration of cement, results in the formation of additional secondary cementitious compounds such as calcium silicate hydrates (CSH) gel that modify the microstructure of concrete and contribute to an improvement in the material's durability. This improvement can be measured in terms of the material's porosity, permeability, and chloride ion diffusivity [29,30].

Unlike industrial by-products such as fly ash, silica fume, and blast-furnace slag, MTK is thoroughly refined to lighten its color, eliminate inert impurities and regulate particle size. MTK particles are typically less than 2 microns in size, which is much smaller than cement particles but not as tiny as silica fume [30]. Furthermore, the usage of MTK in concrete is a good idea [31]. Research has shown that adding MTK to concrete has a significant impact on its mechanical and durability qualities [32,33].

In terms of strength, permeability, and chemical resistance, it was also established that concrete mixes with high-reactivity MTK performed similarly to silica fume mixtures [34,35]. This material is also ecologically benign since it helps to reduce CO_2 emissions into the atmosphere by lowering the amount of ordinary Portland cement (OPC) used [36]. MTK may be used in place of ordinary Portland cement (OPC) in the manufacturing of concrete [37]. The use of MK may drastically reduce cement use which can assist to relieve environmental issues.

Based on the above, the purpose of this study is to provide an overview of the use of MTK in concrete. The qualities of MTK are first discussed, which mostly involve physical and chemical characteristics. After that, the hydration, workability, mechanical characteristics, durability and scan electronic microscopy of MTK concrete are thoroughly examined. Furthermore, the most relevant results and recommendations are offered, which will aid future concrete investigations using MTK. Figure 2 shows a different section of the review.

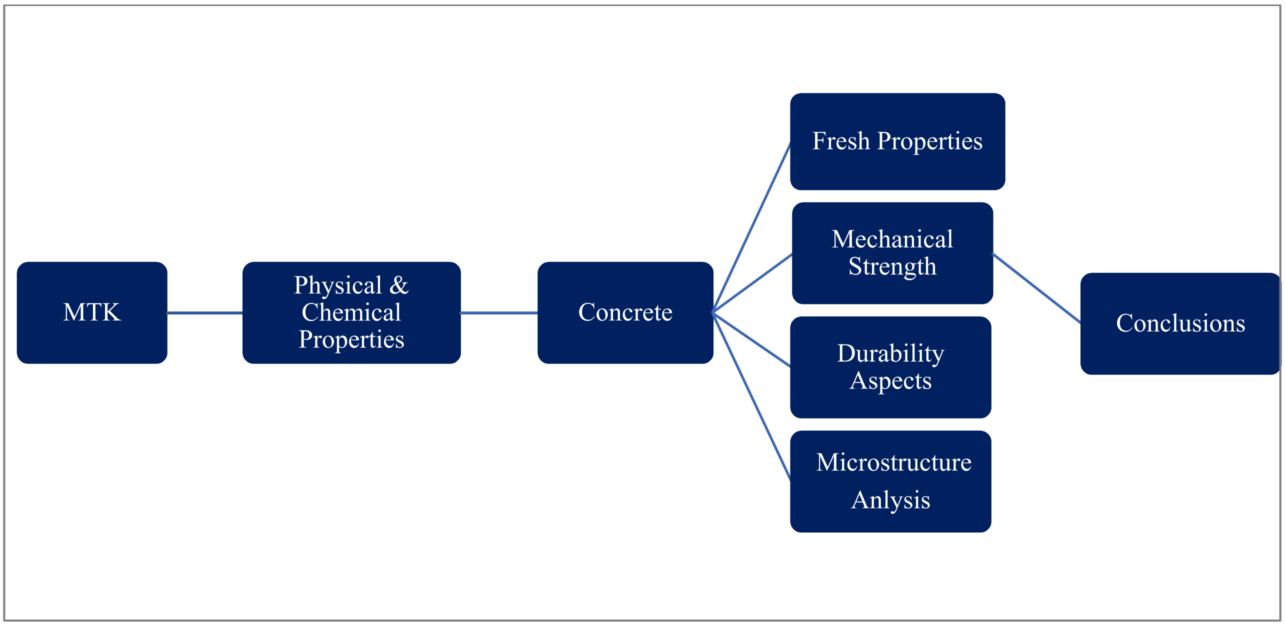

Figure 2. Different sections of the review.

2. Physical Properties

The physical properties of MTK are displayed in Table 1. It should be noted that MTK has a specific gravity of 2.5, which is lower than cement's (3.1 g/cm^3). The color of MTK is normally white as shown in Figure 3a. As demonstrated in Figure 3b, MTK has a multi-modal particle allocation with a mean particle size of 21.44 microns and a D_{90} of 78 microns. Figure 3c displays the MTK's X-ray spectra and mineralogical analyses (kaolinite, hematite, quartz unreactive, and a little quantity of illite) as well as its amorphous phase.

Table 1. The physical properties of Metakaolin (MTK).

Reference	[38]	[39]	[40]	[41]	[42]
Specific gravity	2.5	2.62	2.5	2.5	2.5
Fineness cm^2/g	14,600	-	10,200	-	12,800
Moisture Content (%)	-	-	-	-	-
Specific surface area, (m^2/kg)	-	12,680	-	458	-

According to previous investigations, MTK has the chemical compounds displayed in Table 2. The increased strength qualities are due to the production of additional C-S-H gel due to the high oxide percentages. As per ASTM [29], For a material to be classified as pozzolanic, the total of the three primary oxide ingredients, namely SiO_2, Al_2O_3 and Fe_2O_3 must be at least 50%. All of the MTK samples utilized in the different research projects may be characterized as pozzolanic, according to Table 2 [45].

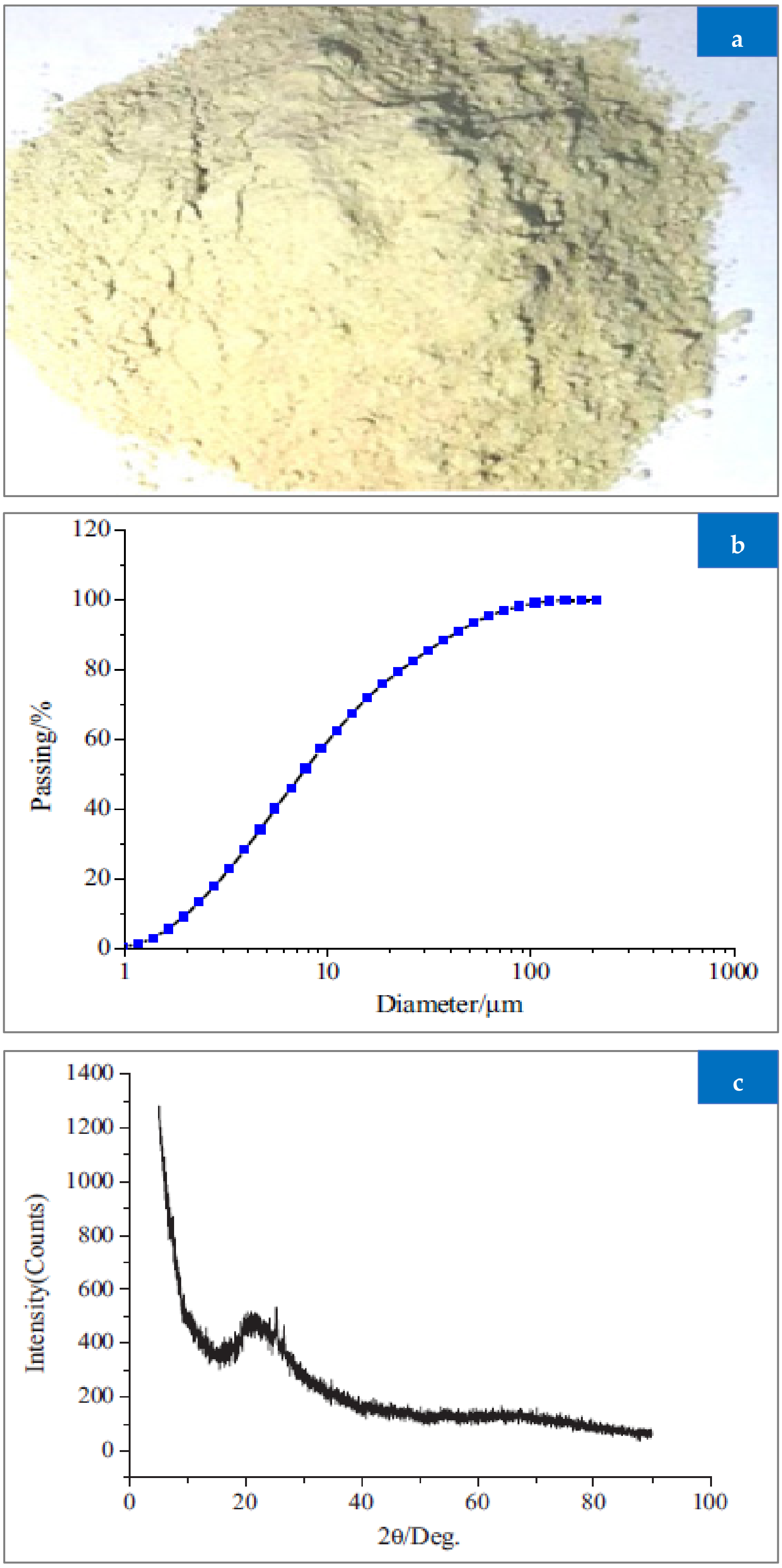

Figure 3. (**a**) MTK [43] (**b**) Gradation Curve of MTK and (**c**) XRD of MTK: Reprinted with permission from [44].

Table 2. Chemical composition of Metakaolin (MTK).

Reference	[43]	[46]	[47]	[38]	[39]
SiO_2	53.26	53.15	54	56.10	53.2
Al_2O_3	43.93	38.44	43	40.23	43.9
Fe_2O_3	0.3	2.65	<1.3	0.85	0.38
MgO	0.49	0.47	<0.8	0.16	0.05
CaO	0.36	0.17	<0.8	0.19	0.02
Na_2O	-	0.08	<0.7	-	0.17
K_2O	-	3.43	<0.7	-	0.10

The gradation curve and morphological features of the MTK sample determine its efficacy as supplemental cementitious material. The engineering qualities of concrete containing MTK are directly influenced by the shape of MTK. Scanning electron microscope (SEM) investigations are the most extensively used tool for determining the morphology of MTK. Morphology serves as a useful material property for assessing the feasibility of MTK as an alternative cementitious material for combating chloride attacks [48]. Figure 4 depicts an uneven and coarse particle surface that reduced concrete flowability because of excessive friction with concrete components.

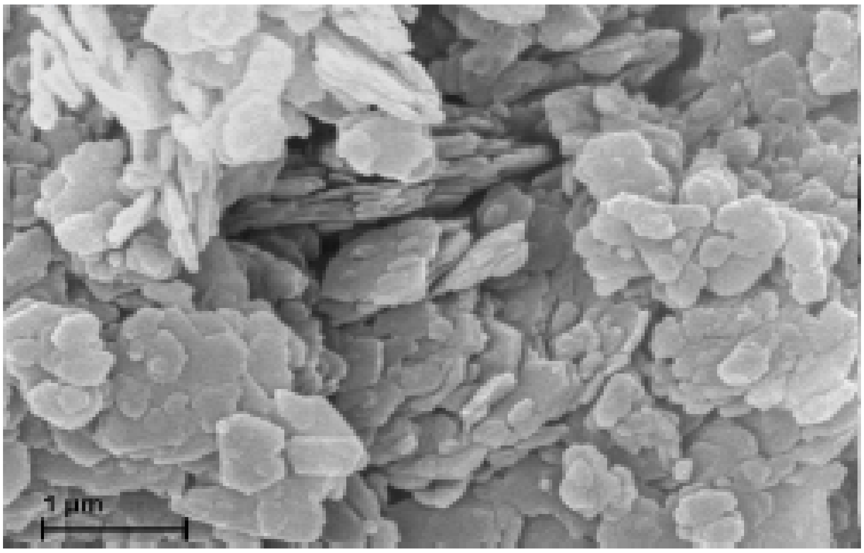

Figure 4. An SEM of MTK Particle: Reprinted from the open access source [49].

3. Fresh Properties

Workability

Workability is described as the smooth with which new concrete may be laid, vibrated, and finished without the component ingredients segregating [50]. The most frequent metric used to determine the flowability of concrete in its fresh condition is a slump. The workability qualities of concrete are directly influenced by particle size distribution, particle shape, water to cement ratio (w/c), temperature, and the quantity of additive supplied to the mix [51]. Figure 5 depicts the slump flow of concrete when MTK is used instead of cement.

The flowability of concrete was seen to diminish when MTK was substituted. The reduced flowability is attributed to MTK's rough surface, which boosted resistance between concrete components, resulting in lower flowability. This loss of workability is due to the MK particles being much smaller than the OPC particles and the fibers themselves absorbing free water, resulting in a slump decrease [52].

MTK had a harmful influence on the flowability of recycled aggregate concrete, according to research (RAC) [40]. The addition of Corban nanotubes and metakaolin to the pastes enhances the plastic viscosity and yield stress [53]. This negative impact is dependent on the MK content since the effect increases as the MTK content increases. The slump of ultra-high performance concrete drops dramatically and MTK particle agglomeration becomes more problematic. As a result of MTK unfavourable involvement in hydration, materials with a homogenous and dense microstructure cannot be created. Based on the findings of the workability and mechanical qualities of ultra-high performance concrete, it can be inferred that a 10% MK content is ideal [54]. At the same dose of plasticizer and water to cement ratio, MTK-blended cement had poorer fluidity than PC with MTK, according to a research [25].

Water requirement rose when MTK dose was raised owing to the larger surface area of the binder containing MTK [55] and the MK's increased responsiveness [56] in comparison to cement. It should be highlighted that the greater the surface area of the binder, the higher the water requirement for OPC with high Al_2O_3 concentration and minimal loss on ignition [57]. Results indicate that depending on their physical and chemical characteristics, MTK may generate significant changes in the flow of mortars. The distribution of the constituent particles' morphologies and the water requirement of MTK are particularly influenced by the kind and amount of contaminants [58]. Superplasticizer was added in greater amounts when MTK was added to concrete, which has a high degree of fineness [59]. To maintain precise standards for the flowability of fresh concrete. Contrarily, using calcite as a substitute for cement in concrete decreased the quantity of superplasticizer required to maintain the particular flowability value [60].

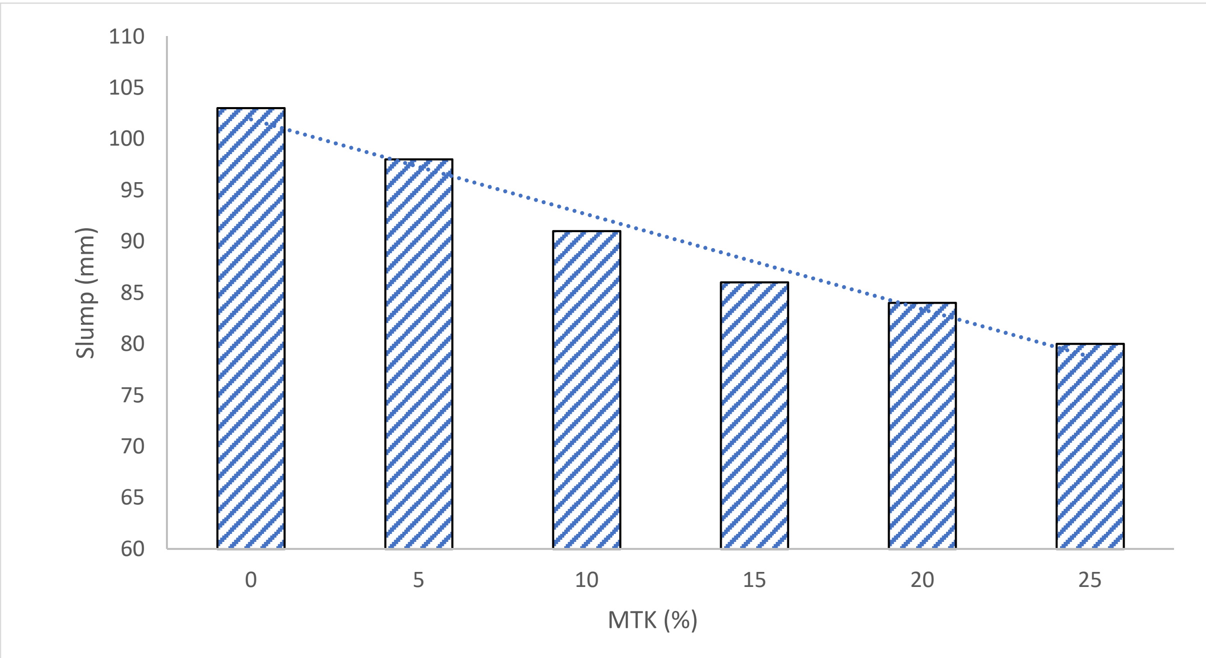

Figure 5. The slump flow of concrete with MTK [61].

4. Mechanical Strength

4.1. Compressive Strength (CS)

As indicated in Table 3 and Figure 6, some studies believe that substituting cement MTK increases compressive strength (CS). It has been discovered that adding the right quantity of MTK to cementitious materials increases their compressive strengths [62]. When the quantity of MTK used exceeds the optimal level, the compressive strength of cementitious materials is reduced.

Table 3. A summary of the compressive strength (CS) of concrete.

Reference	Replacement Ratio of MTK	Optimum	Remarks
[43]	0%, 10%, 15%, 20%, 30% and 40%	15%	Increased
[46]	0%, 5%, 10%, 15%, 20% and 25%	-	Decreased
[39]	0%, 5%, 10% and 20%	-	Increased
[40]	0%, 10%, 20% and 30%	-	Increased
[63]	0%, 5%, 10% and 15%	-	Increased
[54]	0%, 6%, 10% and 14%	-	Increased
[41]	0%, 5%, 10%, 15% and 20%	-	Decreased
[61]	0%, 5%, 10%, 15%, 20% and 25%	15%	Increased
[64]	0%, 5%, 10% and 15%	-	Increased
[42]	0%, 4%, 8%, 16% and 20%	-	Increased
[65]	0%, 5%, 10%, 15% and 20%	5%	Increased
[66]	0%, 5%, 10%, 15% and 20%	15%	Increased
[67]	0%, 5%, 10%, 15% and 20%	15%	Increased
[68]	0%, 5%, 10%, 15% and 20%	15%	Increased
[36]	0%, 10% and 20%	-	Increased
[69]	0%, 5%, 10%, 15% and 20%	15%	Increased
[44]	0%,6%,10% and 14%	10%	Increased

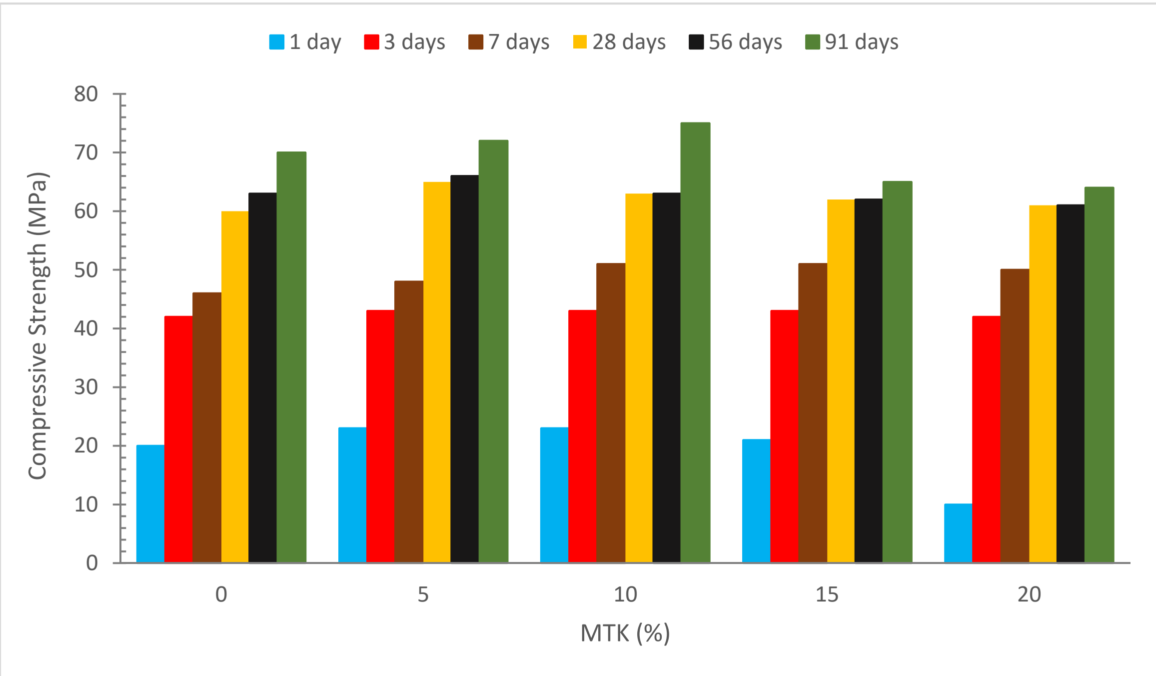

Figure 6. Compressive strength: data source [65].

This is owing to the excess MTK propensity to agglomerate and adsorb around cement particles, causing a delay in the cement's hydration process and a reduction in the calcium trisilicate (C_3S) and calcium disilicate (C_2S) phases in the matrix [70]. Conversely, the increased NMK causes less contact points among cement grains, which function as binding centers [71] and the matrix's dispersion defect causes a weak interfacial transition zone (ITZ) [72]. The CS of concrete uses increasing concentrations of MTK as a partial cement substitute (5, 10, and 15%). The findings depict that as the MTK substitution ratio grew, the CS improved with the 15% substituted specimens producing the best strength values [30].

The clinker dilution effect is used to explain the decrease in CS for 15% MTK as compared to 10% MTK. The diluting effect results from adding an equal amount of MTK to a portion of cement. In MTK concrete, the dilution effects are counteracted by the filler effect, pozzolanic interaction of MTK with calcium hydroxide and compounding effect (synergistic impact of mineral admixture) [73].

Although the mix proportion specifics such as water to cement ratio and the content of MTK, as well as the curing circumstances, are more or less the same, the optimal contents of MTK are not the same, notably the influence of the range of MTK on CS. The different particle sizes and chemical compositions of the multiple MTK specimen used in the analysis may be related to the difference in the optimal MTK percentages recorded throughout all investigation experiments. As a result, further study is required to determine the exact ideal replacement amount, particle size and chemical makeup of MTK for its purpose as a cementitious material.

The strength age relationship of concrete made with partial substitutions of cement with MTK which 28 days control compressive strength is reference concrete as displayed in Figure 7. At 7 days of curing, 10% substitution of MTK show compressive strength 15% less than as compared to 28 days control concrete CS. At 28 days of curing, the CS at 10% replacement of MTK is just 5% more than the reference sample.

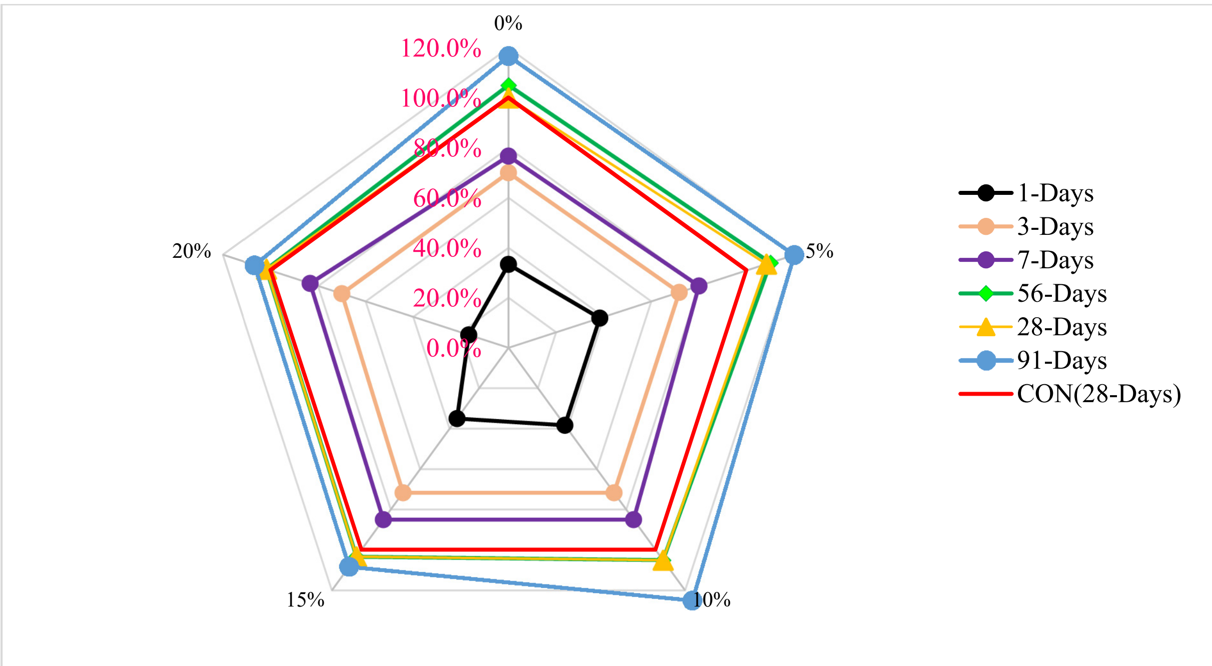

Figure 7. The compressive strength age relation of concrete with different doses of MTK: Data source [65].

The researchers also discovered that after 28 days, there was virtually little strength gain [74]. This is due to the pozzolanic reaction slowing down, which is caused by the total utilization of the calcium hydroxide created during the hydration phase. Nevertheless, at a later age (91 days) considerable improvement in compressive strength (25% more than the reference sample) was observed at 10% replacement of MTK. Therefore, MTK does not improve initial age compressive strength; however, later age (91) compressive strength improved significantly, which was due to the fact that the pozzolanic reaction continued gradually, as it was associated with the hydration of OPC.

4.2. Flexural Strength (FL)

As indicated in Table 4 and Figure 8, some studies believe that substituting cement MTK increases flexural strength (FL). The inclusion of MTK lowers the ultra-high-performance mortar's 1-day mechanical strength. After 14 days, however, all mortars containing 5–20% MTK show stronger compressive and flexural strength than reference concrete [69]. The compression strength (CS) is found to be larger than the FL which may be explained by the fact that the water to binder ratio, mix qualities, aggregate properties, curing circumstances, and age all have varied effects on the compressive and tensile capacity [75]. The impact of MTK in improving the FL of fiber-reinforced cementitious composites (FRCCs) with a water to cement ratio of 0.3 and fiber content of 2% for building surface plastering was investigated by a researcher [76].

Table 4. Summary of Flexural Strength of Concrete.

Reference	Replacement Ratio of MTK	Optimum	Remarks
[40]	0%, 10%, 20% and 30%	20%	Increased
[54]	0%, 6%, 10% and 14%	-	Increased
[61]	0%, 5%, 10%, 15%,20% and 25%	15%	Increased
[64]	0%, 5%, 10% and 15%	-	Increased
[42]	0%, 4%, 8%, 16% and 20%	-	Increased
[65]	0%, 5%, 10%, 15% and 20%	-	Increased
[66]	0%, 5%, 10%, 15% and 20%	15%	Increased
[67]	0%, 5%, 10%, 15% and 20%	-	Increased
[68]	0%, 5%, 10%, 15% and 20%	10%	Increased
[69]	0%, 5%, 10%, 15% and 20%	15%	Increased
[44]	0%, 6%, 10% and 14%	10%	Increased

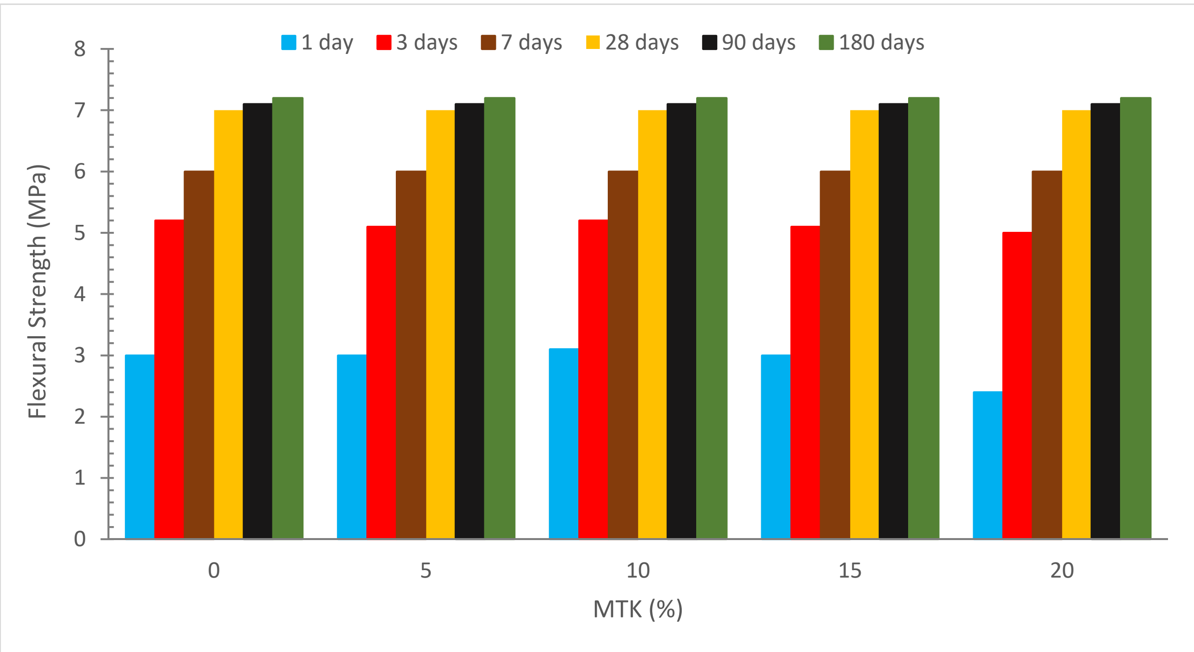

Figure 8. Flexural strength: data source [65].

The findings revealed that, when compared to control FRCC, FRCC with 10% MTK had a 67 percent increase in FL after 28 days, whereas the strength steadily reduced as the MTK contents rose further after 10% [76]. At high temperatures ranging from 400 °C to 800 °C, the compressive and FL of MTK concrete decreased to variable degrees. At high temperatures, however, MTK and fly ash have a strong synergistic impact [77]. The addition of MTK increased the strength performance of ultra-high performance concrete, according to the findings [54].

In comparison to the others, blended mortars containing 10% MTK had the greatest compressive and FL. The interface was reinforced with the boost in curing time and the microstructure of MTK as a consequence of $Ca(OH)_2$ utilization via the pozzolanic reaction of MTK. The blended mortar was denser than the mortar made without MTK [54]. Because MTK is well-known to have strong pozzolanic activity, MTK replacement of 15% offered the greatest outcomes from 3 to 120 days, with steadily rising flexural performance. The typical increases in ultimate strength and strain capacity between 28 and 120 days are 4% and 27%, respectively [38]. When MTK is substituted for cement at a composition of up to 20%, the FL of the mixes with recycled concrete aggregate (RCA) is comparable to that of the control mix. The inclusion of tiny MTK particles and the resulting pozzolanic reaction is responsible for the increased FL of the RCA [78]. Furthermore, the FL of MTK rises and subsequently falls with the replacement rate of MK, which is consistent with the compressive and splitting tensile strength trends [61].

Figure 9 depicts the link between concrete compressive strength (CS) and flexural strength (FL). CS is a function of flexural strength (flexural strength is around 10% to 15% of CS). As a result, as predicted, there is a substantial link between CS and FL. It seems that a regression line is straight. The R square value is more than 90%, indicating that there is a good connection between compressive and flexural strength of varying percentages of MTK at different curing days. The equation may also be used to estimate flexural strength from compressive strength using varying percentages of MTK at different curing days.

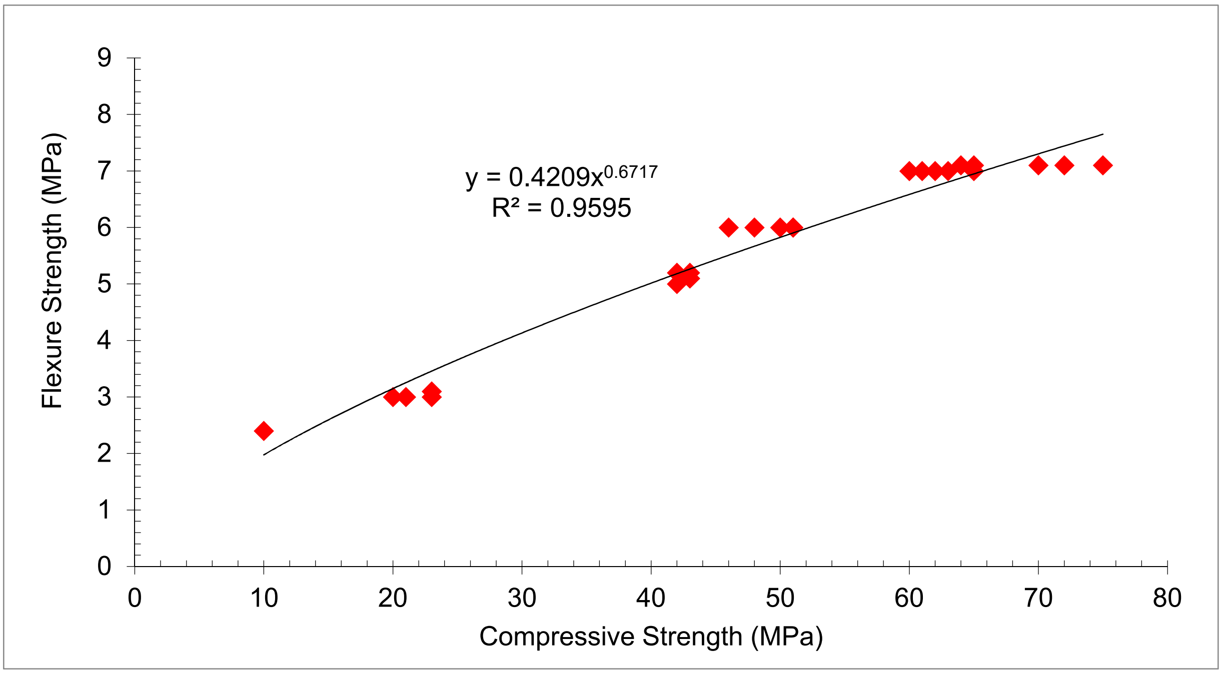

Figure 9. The correlation between CS and FL: Data source [65].

4.3. Split Tensile Strength (STS)

As demonstrated in Table 5 and Figure 10, MTK may greatly increase the tensile capacity of cementitious materials. The maximum values of STS were observed at 10% replacement MTK, following the same pattern as the CS results [63]. MTK content must be optimized for optimal performance. However, several studies have found varied ideal MTK percentages. This is because MTK comes from several sources. The concentration of MTK in the optimal dosing range fluctuates between 10 and 15% by weight of the binder. The results showed that substituting 15% of the cement with MTK improved the mechanical qualities of the combinations [43]. The mechanical strength of concrete improved significantly when 10% of cement was replaced with MTK [68].

Table 5. Summary of the tensile strength of concrete.

Reference	Replacement Ratio of MTK	Optimum	Remarks
[43]	0%, 10%, 15%, 20%, 30% and 40%	15%	Increased
[63]	0%, 5%, 10% and 15%	10%	Increased
[41]	0%, 5%, 10%, 15% and 20%	-	Decreased
[61]	0%, 5%, 10%, 15%, 20% and 25%	15%	Increased
[64]	0%, 5%, 10% and 15%	-	Increased
[42]	0%, 4%, 8%, 16% and 20%	-	Decreased
[65]	0%, 5%, 10%, 15% and 20%	15%	Increased
[66]	0%, 5%, 10%, 15% and 20%	15%	Increased
[68]	0%, 5%, 10%, 15% and 20%	10%	Increased
[36]	0%, 10% and 20%	10%	Increased

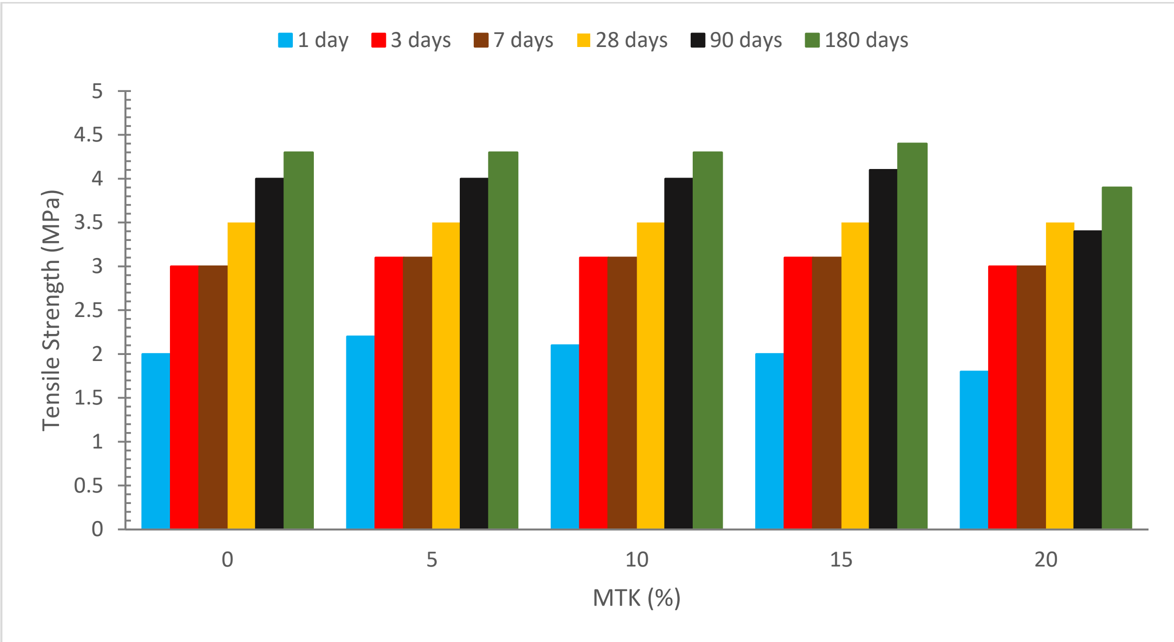

Figure 10. Tensile strength: Data source [65].

According to research, adding 2 percent and 5 percent MTK to reactive powder concrete enhanced the strength for 7 and 60 days by 3.04 to 3.41% and 6.95 to 7.98%, respectively [79]. The research found that the STS of concrete containing 3% MTK at a water to binder ratio of 0.53 cured for 7 to 90 days was not considerably enhanced and was slightly lower or comparable to the strength of control concrete [80].

The findings indicated that 15 percent MTK and polyvinyl alcohol fibers significantly improve the performance of RAC. The STS and FL enhancements were more substantial in terms of mechanical characteristics. Internal holes and fibers of RAC with a 15% MK substitution rate were greatly decreased, and a considerable volume of calcium silicate hydrate (C-S-H) gel was produced within RAC, which had the best fiber adhesion. The most substantially improved performance was thought to be RAC with PF and 15% MTK [61].

The pozzolanic action of MTK which fills fractures, interconnecting pores, and micro-pores in the ITZ and increases the matrix's internal compactness, is primarily responsible for the increase in STS [81]. However, according to the findings of the research, adding MTK reduced the STS of the mixtures. The most significant reduction was seen in the mix with the lowest water to cement ratio. The low specific surface area of MTK, which was only 20% greater than that of Portland cement, is again to blame for the drop in STS [41]. Therefore, the review suggests more detailed investigation is required for the STS of concrete with MTK substitutions.

Figure 11 shows the relationships between CS and STS of concrete with substitution MTK instead of cement. The relationship between the mentioned two strengths was developed using experimental data from CS and STS testing as per a past study [54]. Figure 12 may be used to create a regression equation using linear regression analysis. It can be noted that the CS and the STS of the MTK-based mixes have a strong correlation coefficient with an R square value greater than 0.90.

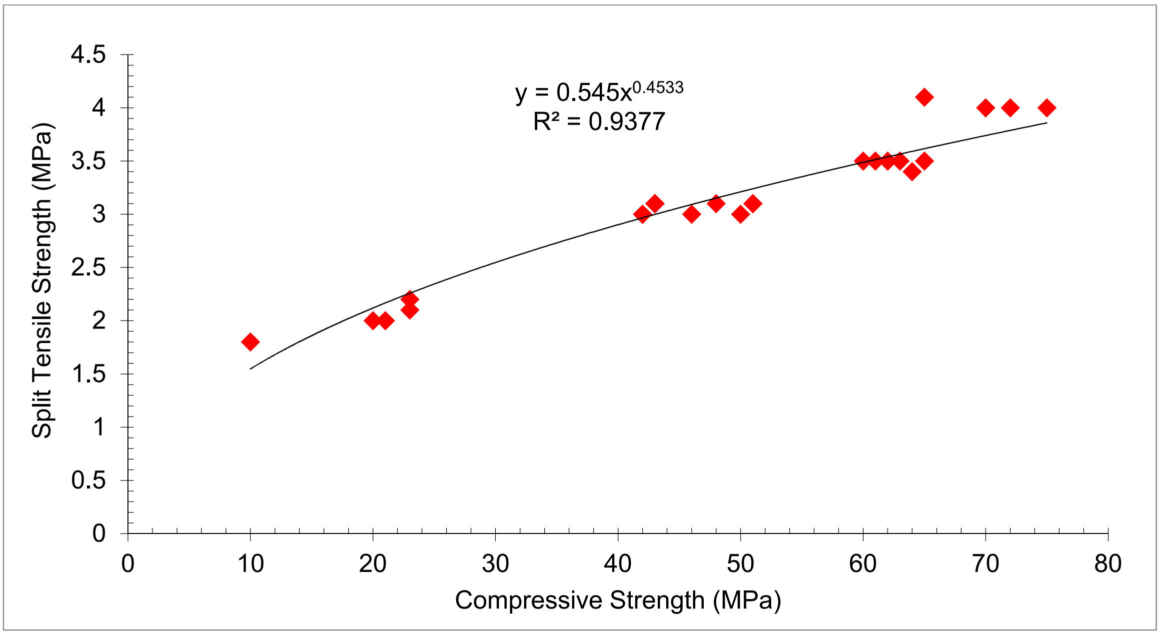

Figure 11. The correlation between compressive and tensile strength: data source [65].

5. Durability

The ability of a concrete structure to withstand harsh exposure conditions for the remainder of its service periods with no excessive failure of usability or the necessity for refurbishment plans is referred to as durability. Concrete's durability is linked to its performance, which means that it may be resilient in one atmosphere but not in a different [12].

5.1. Chloride Ion Penetration

The degradation of reinforced concrete maritime constructions has an influence on daily life in terms of safety, economics, and sustainability [82]. The unnecessary quantity of concrete manufactured to restore and revitalize deteriorating concrete rather than being utilized in new building plans places a significant economic burden on society. Coastal engineers must thus be aware of the aspects that impact the prolonged-term sustainability of marine concrete constructions.

The principal issue impacting the permanence of reinforced concrete buildings in maritime and seaside areas is chloride assault [83]. Chloride ion penetration into concrete is also important for the physical and chemical processes that lead to concrete microstructure degradation and steel reinforcement corrosion [84]. As a consequence, maritime constructions become dangerous and have a shorter service life. When a threshold concentration of chloride ions has collected at the steel reinforcement, the corrosion process begins [85]. The degradation of steel in buildings produced by chloride-induced corrosion is claimed to be a serious durability issue not just in South Africa, but across the globe [82].

The MTK concentration and curing age increased and the chloride resistance of concrete improved. According to research, mixtures containing 5% and 10% MTK demonstrated better resistance to chloride permeability [86]. The concrete design with the highest chloride resistance was created by adding MTK to concrete and using artificial seawater as blending water. With the pozzolanic reaction and filling voids effect of MTK and acceleration of hydration by saltwater, the addition of MTK and seawater increased the microstructure of the concrete. At 18 mm, there were less fine corrosion products indicating that combining saltwater with metakaolin enhances concrete chloride resistance while limiting the influence of chloride intrusion in the microstructure [87]. The double-layer structure and pozzolanic action of MTK efficiently prevented chloride ions from penetrating, according to research [20]. The pozzolanic reaction, which enhanced the binding qualities of cement paste and therefore increased resistance to chloride penetration, the MTK improved chloride resistance. The density of concrete was also improved, owing to the micro filling effect which filled the spaces, resulting in greater resistance against chloride assaults.

5.2. Water Absorption

Figure 12 describes the water absorption capacity with different percentages of MTK ranging from 0% to 30% in 5-percent increments. The pozzolanic activity and filling voids of MTK, and concrete water absorption were reduced when cement was replaced with MTK. The impact of varied MTK 2 to 14 percent levels on the water absorption of cementitious materials was examined in research [88]. The findings revealed that MTK reduced the water absorption capacity of the matrix to varying degrees. When the MTK concentration was more than 6%, however, the beneficial effect rapidly faded [88].

According to particular research, MTK decreased the water absorption of concrete by 16.5 to 25% when compared to a control sample [80]. The research found comparable findings, indicating that the mortar with 10% MTK and 5% silica fume had the lowest water absorption [89]. The filling effect of ultrafine MTK and its pozzolanic reaction, according to research, is what causes the decrease in water absorption [36].

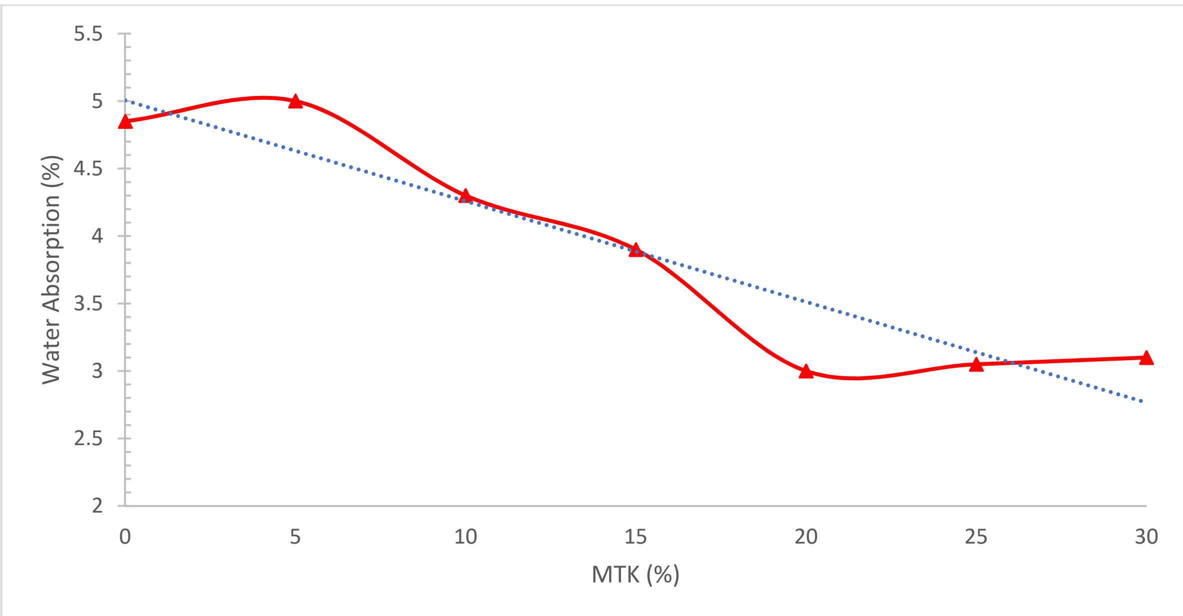

Figure 12. Water absorption [90].

5.3. Porosity and Water Sportivity

The average effective porosity and water sportively fall of the mixture with incorporating MTK as compared to the reference samples as presented in Figure 13. The 10% MTK mix had the smallest mean water sportively outcomes, whereas the 15% MTK mixture had the least mean effective porosity. MTK capacity to fill the voids of aggregates is largely accountable for the concrete's normal porosity and water resistance [91]. The 10 percent, 15 percent, and 20 percent MTK specimens were found to give tremendous air permeability defense, whereas all MTK-containing specimens gave acceptable water permeability protection. The water absorption increased as the MTK percentages improved, which contradicts the findings of the water sportively and porosity test which showed that the 10% MTK and 15% MTK samples generated the lowest water sportively index and average effective porosity, respectively. Human error during the testing technique and defective equipment are two possible explanations [92]. At 28 days of curing, the cement plates with the addition of 5 to 20% MTK show a similar porosity. However, increasing the MTK dose reduces the most likely pore radius, showing that the pore structure is favorably refined [69].

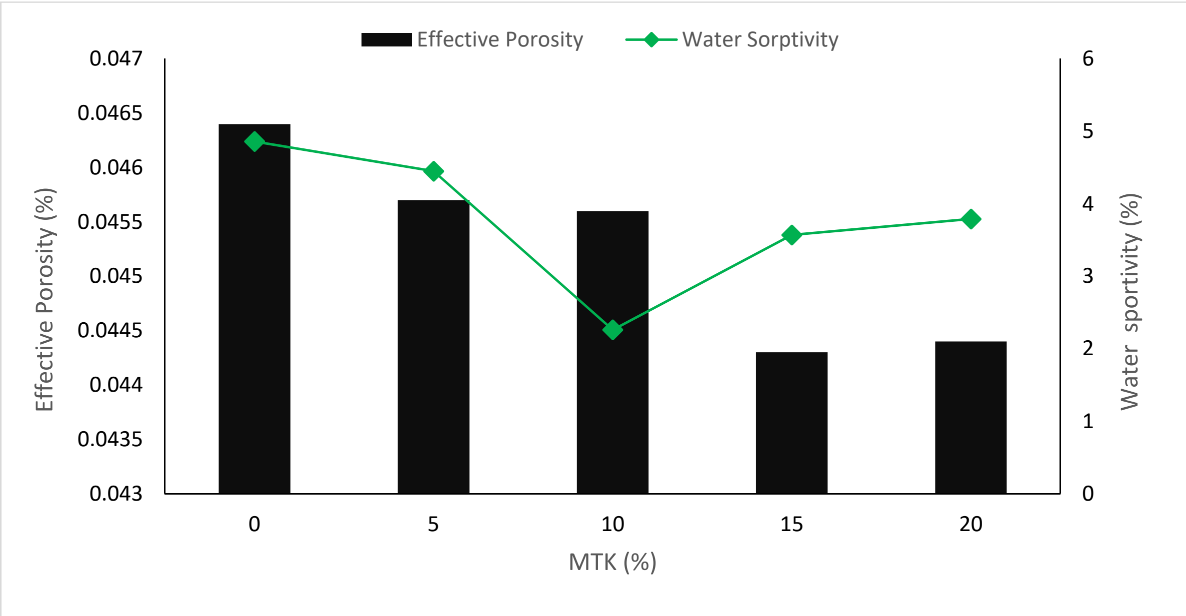

Figure 13. Porosity and water sportively [92].

5.4. Permeability

The size, volume, and connectivity of a material's pore system, which in turn depend on the type of binder used and how hydrated it is, as well as the presence of aggregates (such as in the case of haloes transition) and fines, whether reactive or not, all, play a role in a material's permeability to a cementing matrix [93]. Permeability of chloride ions also effect the reinforcement durability due to corrosion [94].

This characteristic determines a material's resistance to the penetration of hostile chemicals and, therefore, its durability [95]. This low permeability is also of significant importance for the creation of gas- and water-tight containers, coatings, and storage facilities for radioactive waste.

The lowest coefficient of permeability was found at a 15 percent replacement level as shown in Figure 14. This may be a consequence of the pores being filled with hydration products, which would lead to pore refinement and increased concrete performance [96].

Concrete sorptivity is comparatively decreased when metakaolin is added [97]. The decrease in permeability due to the addition of pozzolanic materials can be attributed due to pozzolanic reaction and micro filling which give more dense concrete [97]. The conventional concrete exhibits a sorptivity of 0.114 mm/min$^{0.5}$, whereas the sorptivity ranges from 0.062 to 0.097 mm/min$^{0.5}$. Comparing concrete specimens with commercial metakaolin (MKC) to specimens with MTK, MKC-concrete exhibits the best behavior, while concrete with MKC and 20% replacement of sand exhibits the lowest sorptivity [29].

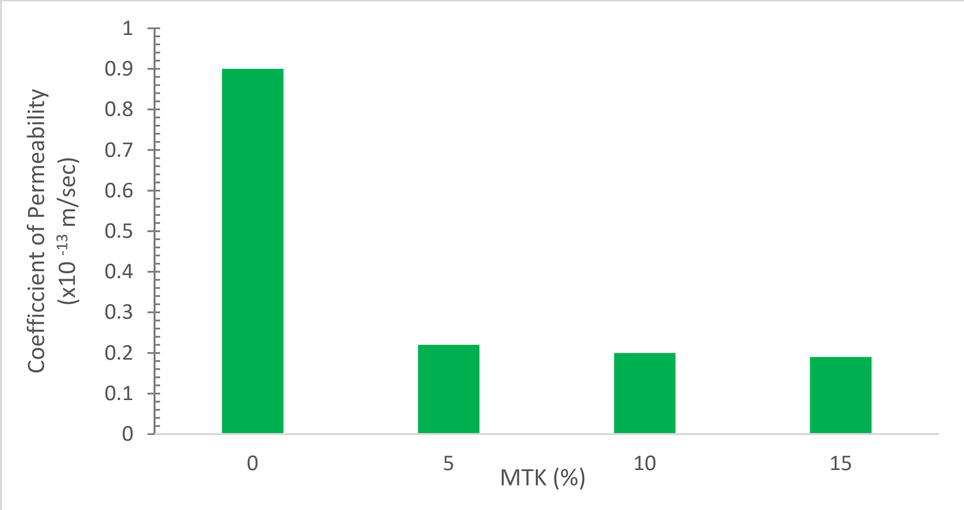

Figure 14. Permeability: data source [63].

6. Microstructure Analysis

6.1. Pozzolanic Activity

The thermogravimetry (TG) and differential scanning calorimetry (DSC) curves of MTK paste at 28 days are shown in Figure 15. The DSC study traces as a function of temperature for MTK–CH paste reveals four distinct zones of evident mass loss, which correlate to four distinct peaks. The first peak, which occurs at about 90 °C is mostly because of the desorption of calcium silicate hydrates (CSH) and stratlingite (C_2ASH_8) physiosorbed and interlayer water molecules [98]. The grafting process of C_2ASH_8 interlayer anions correlates to the second dehydration peak, which occurs at 165 °C. Dihydroxylation of lattices and breakdown of C_2ASH_8 interlayer anions results in the third peak at 215 °C [99]. The fourth peak, at 670 °C, is caused by $CaCO_3$ decomposition [100].

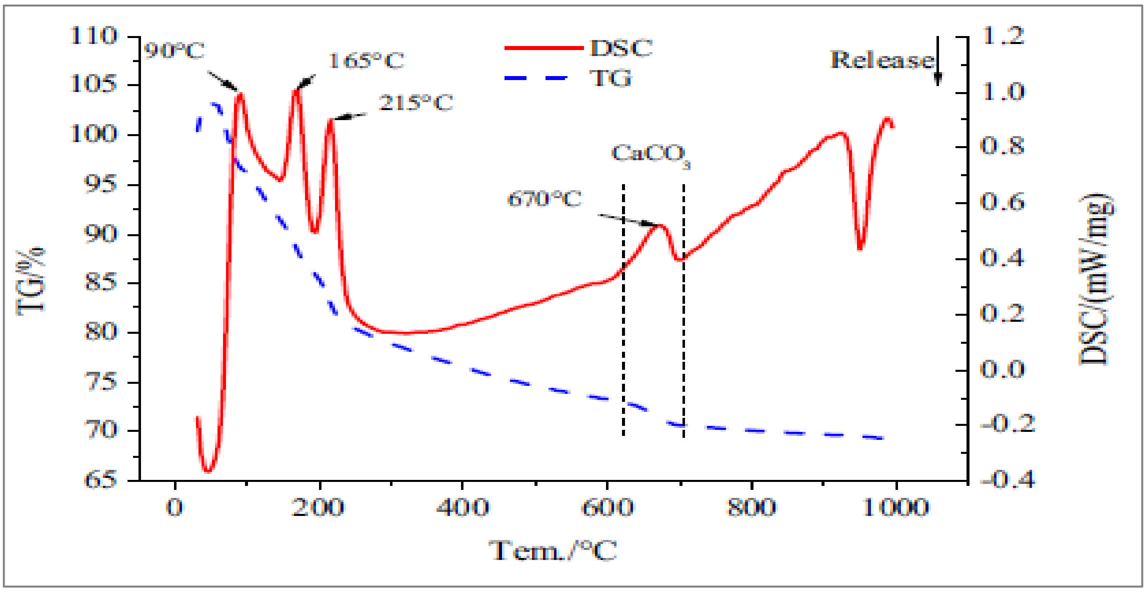

Figure 15. DTG of MTK: Reprinted with permission from [44].

The time histories of variations in pozzolanic reactivity for the MTK specimens are shown in Table 6. It is evident that the majority of calcium hydrate (CH) has not responded to MTK after three days. MTK pozzolanic reactivity index is 23.2 as a consequence. The pozzolanic reactivity index of MTK increases by 13.7 days compared to 3 days as hydration increases. Table 6 further reveals that a rapid spurt of reaction in MTK–CH mixed samples between 7- and 28-days results in elevated pozzolanic reactivity indices of 94.3. A study claimed that MTK has a 22.6 greater pozzolanic reactivity index than silica fume after 28 days, which is the greatest variation between all curing periods [44]. This conclusion that MTK pozzolanic reactivity develops rapidly after 7 days is consistent with the findings of the research [101].

Table 6. Pozzolanic activity results: Reprinted with permission from [44].

Time (days)	$Ca(OH)_2$	$CaCO_3$	Total $Ca(OH)_2$	Reactivity Index
3	7.39	4.21	38.41	23.2
7	7.01	1.46	31.56	36.9
28	0	1.68	2.89	94.3
56	0	1.45	2.46	95.1

The heat needed for the breakdown of the CSH and CH stages as a function of MTK percent is shown in Figure 16. The heat of decay of CSH enhances as the quantity of MTK enhances while the heat required for the decay of CH decreases, indicating that the mortars modified with MTK have a high degree of hydration. Furthermore, as a consequence of MTK's use of CH, the quantity of heat needed for its breakdown is reduced. The pozzolanic reaction with MTK causes the CH phase released during hydration of MTK-controlled cement to have a crystalline structure (i.e., eroded crystals), as shown by the reduction in CH enthalpy. Because amorphous hydration products have stronger strength qualities than crystalline hydrates, the hardened cement made with MTK substitution has a denser structure than the plain cement paste [97].

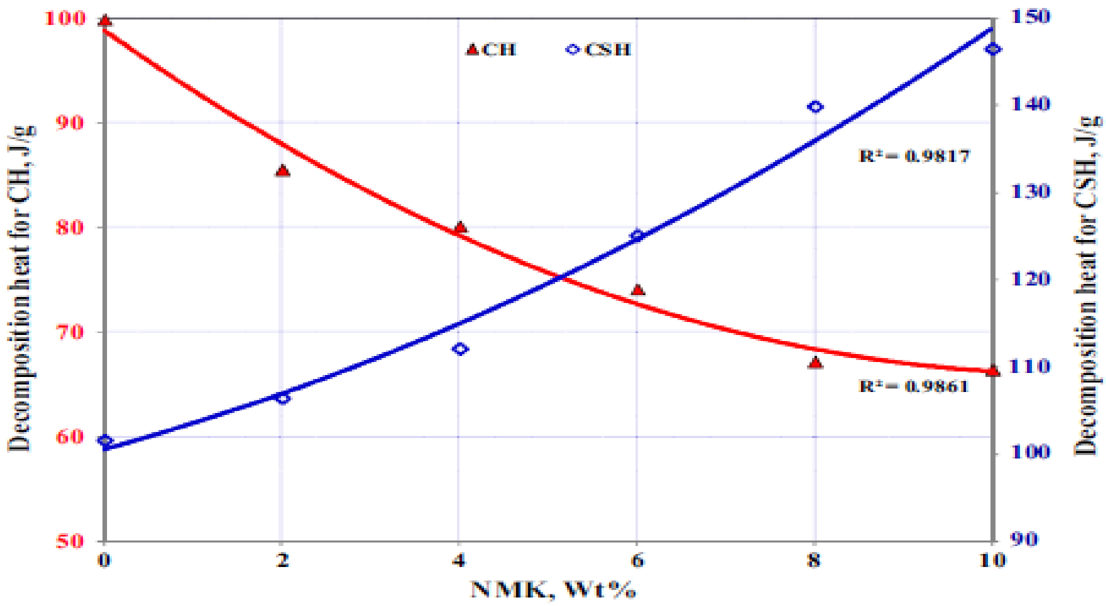

Figure 16. CH conversion into CSH: Reprinted with permission from [88].

6.2. Heat of Hydration

The experimental findings of controlled heat flow and cumulative heat developed of various MTK mixed mortars are displayed in Figure 17. The hydration heat of new mortars may be detected using an isothermal calorimeter for up to 100 h. The findings in Figure 17a reveal that the normalized heat flow is in the range of 6% > 0% > 10% >14 percent. In other terms, temperature increases in concrete buildings follow the same pattern as heat transfer, particularly at large scales. As a result, the mortars containing 6% MTK in this study produce more microfractures and shrinkage than the others. When cementitious materials with strong pozzolanic reactions, such as MTK and silica fume react with hydrated CH, the hydration rate increases, contributing to the pozzolanic reactivity's exothermal impact [98]. The increased hydration rate has an impact on the durability of mortars and concrete, mostly owing to shrinkage and the production of tiny fractures. A study [99] conclude that the accelerated impact of MTK on cement hydration was blamed for the higher temperature increase of MTK blended mortars compared to pure cement-based mortar.

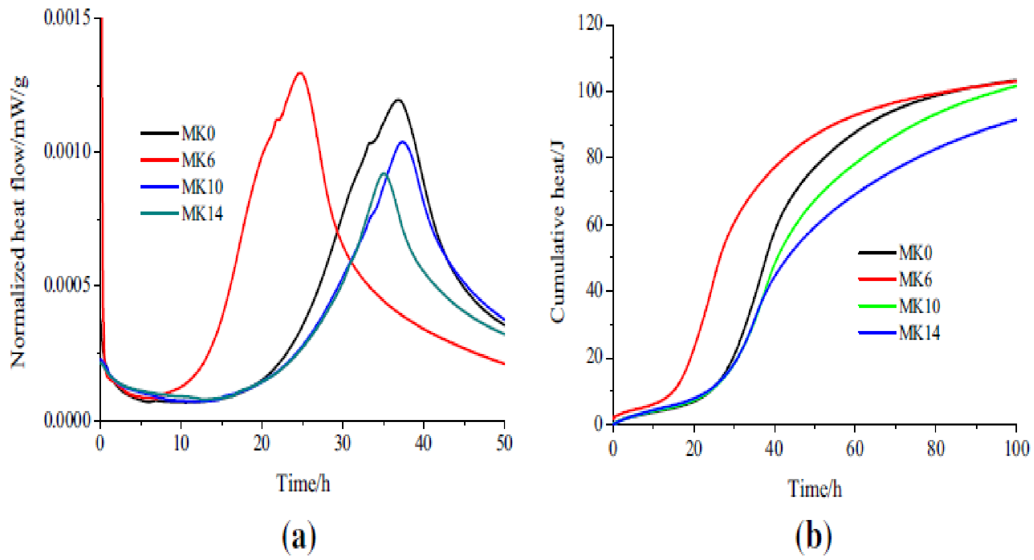

Figure 17. Heat of hydration with MTK (**a**) Normalized and (**b**) Cumulative Heat: Reprinted with permission from [44].

Zhang et al. [34] concluded that the temperature increase was due to MK's strong reactivity with CH. Nevertheless, there is a strong indication that cementitious materials (MTK), which react with calcium hydrate (CH), have a role in early heat released by speeding up the hydration of Portland cement and swiftly interacting with CH produced during cement hydration [34]. A combination with 14 percent MTK inclusion is favorable in terms of temperature increase. However, given the importance of mechanical strength in this study, 10 percent MTK is more useful in engineering than 14 percent MTK. The cumulative heat developed for 100 h of various MTK concentrations is 103.32, 103.03, 101.74, and 91.58 J, as shown in Figure 17b.

The overall heat evolved falls as the MTK content rises. When compared to mortars with 6 and 10% MTK, the heat generated by a 14 percent MTK amount mortar is much lower than that of a mortar without MTK. This is because, despite the accelerated impact of MTK on cement hydration, the cement mass is insufficient to create enough CH to react with pozzolans. The accelerating impact on cement hydration and the pozzolanic interaction between MTK and hydrated CH are both reasons why mortars with 6 and 10% MTK produce comparable heat to mortars with 0% MTK [74].

In addition, Figure 17b shows that the acceleration period for 6% MTK begins at 5 to 6 h, while MTK 0%, MTK 10% and MTK 14% all begin at 10 to 11 h. As a result, it can be stated that only mortars containing 6% MTK have an acceleration impact on cement hydration. This might be because of the water-absorbing impact of MTK hydrophilic characteristic which causes the cement to take longer to hydrate. The negative impact of MTK on cement hydration, on the other hand, is advantageous in reducing the likelihood of shrinkage and micro-fractures which improves the durability and service life of MTK-based cement concrete.

6.3. Scan Electronic Microscopy (SEM)

The findings of the SEM investigation of the MTK-containing concrete samples are shown in Figure 18. It is clear that there are several big fragments present that may be categorized as anhydrate clinker grains. These particles are linked to the hydration process in which the smaller clinker grains dissolve first, followed by the bigger grains [101]. In the microstructure of the concrete sample, numerous tiny voids, haphazardly shaped capillary spaces, and circular holes were discovered.

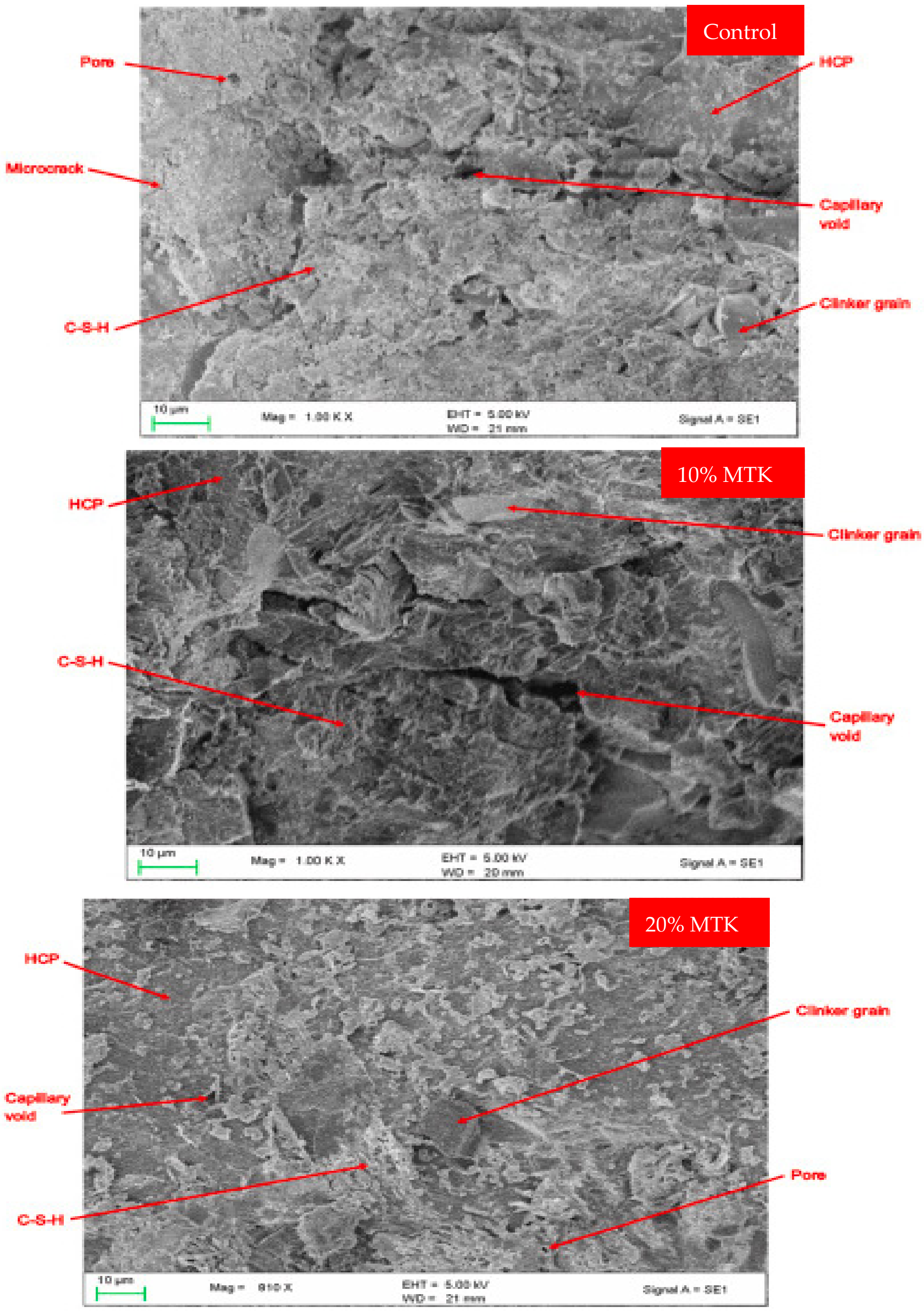

Figure 18. An SEM of concrete with MTK [92].

The presence of the aforementioned sub-structures has a harmful influence on concrete's strength and permeability. When the MTK content rises, the size and appearance of tiny cracks, capillary cavities, and openings shrink. This is due to the fact that MTK improves the porous structure of the matrix by filling up the spaces among the aggregate particles which is consistent with the microstructural findings achieved by MTK [87].

A study also claimed that the increased percentages of MTK result in denser concrete, particularly interfacial transition zone (ITZ). However, the addition of MTK beyond 10% results in cracks (14% substitution of MTK) which adversely affect concrete performance [54]. Similar, the influence of the sand particles' interlocking structure was decreased because the spaces in the calcareous sand were filled with calcium carbonate. Therefore, the pozzolanic reaction and filling voids of MTK results in a denser structure which ultimately improved concrete strength and durability properties. However, a higher dose of MTK results in harmful effects due to a lack of flowability which causes more voids in concrete.

7. Conclusions

A comprehensive investigation of the performance parameters of concrete incorporating MTK as a partial cement substitute was provided in this review article. Physical and chemical properties of MTK, flowability, strength, durability, SEM and heat of hydration characteristics of concrete were all evaluated in this review. The following findings were drawn from the study:

- Physical properties of MTK show rough surface texture which adversely affects the slump flow of concrete.
- The chemical composition of MTK indicates that MTK has the potential to be employed as a cementitious material.
- Increased the workability of concrete with the incorporation of MTK.
- The heat of hydration declined as the percentage of MTK increased. This is owing to the fact that the pozzolanic response is slow.
- Pozzolanic activity of MTK shows an increase in CSH concentrations which improved the binding properties of concrete.
- Mechanical performance such as compressive, flexural and tensile capacity improved significantly with the replacement of MTK. The highest compressive capacity was obtained at a 10% substation of MTK which is 25% more than the control sample (28 days). However, the optimum amount is important. Based on the review, the optimum dose differs from 10 to 20% changing on the basis of MTK. It can be also noted that the enhancement in the initial age mechanical performance of concrete with MTK was not significant. However, at a later age (91 days) considerable improvement in strength was observed.
- An increase in durability performance of concrete with MTK was observed up to some extent but less information is available.
- SEM results confirm the micro filling creditability MTK which gives more dense concrete.

8. Recommendations

- Thermal activation of MTK to improve further its pozzolanic activity should be explored.
- The creep and shrinkage properties of concrete with MTK should be investigated.
- Detailed study on durability characteristics of concrete (particularly acid attacks) with MTK should be investigated.
- No data is available on the alkali-silica reaction (ASR).
- Thermal assets such as thermal conductivity and heat insulation with MTK should be investigated.

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