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Ideal supplementary cementing material – Metakaolin: A review

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ABSTRACT

Though being an ancient trend, usage of the homogeneous material cement in the construction industry is steadily getting eradicated with the springing up of supplementary cementing materials (SCM). Metakaolin is an imminent mineral admixture extracted from the mineral ore kaolinite, which enhances the interfacial zone by more efficient packing at the cement paste-aggregate particle interface, thus reducing the bleeding and producing a denser, more homogeneous transition zone microstructure. This paper depicts the various repercussions of the pozzolanic material metakaolin in the fresh and hardened properties of concrete when replaced with cement in finite amount. Also, it states the behavior of high-performance concrete and self-compacting concrete with metakaolin.

KEYWORDS

metakaolin, kaolinite, pozzolanic materials, self compacting concrete, high performance concrete

1. INTRODUCTION

Metakaolin (MK) is the anhydrous calcined form from the clay mineral kaolinite. It is a manufactured product rather than a by-product. It is formed when china clay (mineral kaolin) is heated to a temperature between 600 and 800 °C. Its quality is controlled during manufacture, resulting in a much less variable material than industrial pozzolans that are by-products. In the 1960s, metakaolin was first used in Brazil for construction of large dams. The original intention was to suppress the damage due to the alkali-silica reaction, which induces swelling of concrete by adsorbing water from the surrounding. The particle size of metakaolin is smaller than that of the cement particles but not as fine as silica fume.

2. IMMINENT MINERAL-METAKAOLIN

Being the most effective pozzolanic material, it is available in many different qualities and varieties. It is a well known admixture even in the '90s, nevertheless, is very commonly used in the present decade by many researchers throughout the globe. Metakaolin inhibits a high equivalent quality of cement, and hence it is often referred to as High Reactivity Metakaolin (HRM). The non-reactive impurities in metakaolin are removed by water processing leaving the 100% reactive pozzolan behind [56]. Apparently, the kaolinite mineral (china clay) ores are spread throughout the continents and most of the sources were seemingly in China, which incites the Chinese people for the vast usage in vessel making and architectural works.

2.1. Metakaolin in mid '90s

Though few formulations were flourishing in the '80s on metakaolin, an exaggerated analysis unfolded steadily in the pop up of 1990s. Wild et al. [59] detailed the portlandite content at different ages through thermogravimetric analysis relating it to the relative strength, keeping

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the cement mortars and pastes with 0, 5, 10 and 15% replacement of cement with MK and with a water/binder (w/b) ratio of 0.55. The removal of portlandite by pozzolanic reaction reached a maximum at about 14 days, along with a hike in relative strength in the MK mortars and pastes. Wild et al. [59] stated three primary factors that influence the contribution of MK to the concrete strength when it is partially replaced for cement in concrete. They are listed as the filler effect, acceleration of the OPC hydration and the pozzolanic reaction of MK along with Calcium Hydroxide (CH). Thus, the obtained results exhibit 20% wt of MK as the optimum Ordinary Portland Cement (OPC) replacement level and the enhancement of strength are limited to 14 days. Khatib and Wild [30] determined the pore structure and the intruded pore volume by conducting mercury intrusion porosimetry. Metakaolin in cement paste further refines the pore structure; the refinement process appears to wind up at 14 days, which in turn shows a maximum relative strength and a minimal rise in the total pore volume along with the CH level. Palomo et al. [46] studied the alkali activation of MK and it is with the aggressive solutions. Sand and alkali-activated MK is cast into prisms immersed in sodium sulfate solution (4.4% wt), deionized water, ASTM sea water, and sulfuric acid solution (0.0014). At 7, 28, 56, 90, 180, and 270 days, the prisms were removed from the solution. For physical, mechanical and microstructural analysis, the porosity, flexural strength, and X-ray diffraction tests were conducted. Good stability is recorded for the resultant hydroceramic for up to 270 days when submerged in various types of aggressive liquids. Faujasite crystals tend to act as a reinforcement of the cement mortar. Curcio et al. [14] compared and studied four commercially available MK samples with silica fume. Three among the four samples developed an elevation in compressive strength that of silica fume at early ages. The plotted results from the thermal analysis depict that water loss is due to the variation of the hydration products obtained and on the permeability of the materials, which can be related to the fineness of the micro-filler in the casted specimens with MK. Bai et al. [5] combined pulverized fly ash and MK to partially replace it for PC and study the workability of concrete. Vee Bee time, Slump, and compaction factor tests were performed for measuring workability. With an increase in MK content Workability of MK-PC concrete is eventually reduced. When super-plasticizer is used at low w/b ratio (=0.4), there is a critical MK/PFA ratio (~0.4) above which workability declines and below which workability tends to increase with high replacement level. Terrence [52] evaluated the efficacy of metakaolin in minimizing the expansion due to alkali-silica reaction (ASR). When HRM is used to replace up to 20% of OPC the alkali concentration of the pore solutions from pastes is significantly low.

Table 1. Chemical composition of cement and metakaolin

Chemical composition	Cement (%)	Metakaolin (%)
Silica (SiO_2)	17–25	50–60
Alumina (Al_2O_3)	3–8	30–40
Magnesium oxide (MgO)	1–3	0–2
Potassium oxide (K_2O)	0–1	0.5–1.5
Sulfuric anhydride (SO_4)	1–3	1–3
Calcium oxide (CaO)	60–65	0–0.5
Ferric oxide calcium oxide (Fe_2O_3)	0.5–6	0.5–5

Table 2. Physical properties of cement and metakaolin

Physical parameter	Cement	Metakaolin
Color	Grey	Off white
Physical form	Fine powder	Powder
Loss on ignition	1.3	0.68
Specific gravity	3.15	2.5

2.2. The analogy between the properties of cement and metakaolin

The rogue chemical composition (Table 1) of metakaolin enables the material to behave itself as the ideal supplementary cementitious material among other minerals and byproducts that are in practice at present. Metakaolin is produced by thermally activating high purity kaolin clay within a specific temperature. The heating process spills out water from the kaolin ($Al_2O_3.2SiO_2.2H_2O$) and alters the material structure resulting in an amorphous aluminosilicate ($Al_2O_3.2SiO_2$), metakaolin.

Metakaolin, when combined with Portland cement, reacts rapidly with CaOH that is released from the hydration of cement to develop various hydrates namely C–S–H, C_2ASH_8 – stratlingate and C_3AH_6 – hydrogarnet [23].

2.3. How metakaolin outbalance other SCM's

Amidst many mineral admixtures accessible, metakaolin is a mineral admixture whose prospects have not yet been fully tested and only finite studies have been carried out in India on the use of MK for the development of high strength concrete [49] [42]. It is obtained from natural deposits of kaolin by thermal treatment. Due to high surface area and amorphous structure (Table 2) MK shows high pozzolanic reactivity. Incorporation of MK in concrete has improved the performance of concrete under various conditions. Also, the ultrafine MK enhanced substantially the pore structure of the concretes and reduced the content of the harmful large pores, hence making concrete more impervious, especially at the replacement level of 20% [24].

2.4. Metakaolin ores in India

Kaolinite, the mineral ore for metakaolin in India as per United Nations Framework Classification for Resources (UNFC) system is mentioned at 2,705.21 million tonnes. 70% out of the total reserves are under proved type, and about 53 million tonnes (30%) reserves categorized as probable type. The resources are scattered in a number of states, out of which about 25% is found under Kerala, followed by Rajasthan and West Bengal (16% each) and Karnataka and Odisha (10% each). Out of total resources, about 608 million tonnes (22%) are categorized as ceramic pottery grade, 4% falls under chemical, paper filler and cement grades, and about 1,980 million tonnes (73%) resources are classified as mixed grade, unclassified, others & not-known categories [27] (Part-III: Mineral Reviews)

3. FRESH CONCRETE PROPERTIES WITH METAKAOLIN

Metakaolin is one among the artificial pozzolanic admixtures that are presently used in a variety of mortar and concrete mixes. Its effect and its behavior are highly dependent on its activity and also on formulation features like workability and the method of mixing in the formulation [45].

3.1. Workability

In pursuance of good dissipation of the MK, the definite amount of MK and super-plasticizer were mixed with water to produce slurry which is then added to the coarse aggregate and mixed for a minute [20]. The fine aggregate was then combined and mixed for a couple of minutes followed by the cement and mixed for further two more minutes. For the lower workability control mix, additional vibration was used to make it fully compacted [59].

The workability of MK-PC concrete is considerably diminished with inflation in MK content. The high chemical activity and high specific surface lower the workability which in turn elevates the water uptake and thus there is a higher water requirement. The influence of MK on flow and compaction is ceased by the incorporation of superplasticizer. This is ascribed to the thixotropic nature of clay suspensions and lower void space due to the higher dispersion of MK particles [5]. Workability was observed to cease with 15% of MK for which finite amount of super plasticizer is much needed to counterbalance it [47].

3.2. Setting time

Replacement of OPC by MK up to 20% prolong the initial and final setting time of cement mortar since the MK particles develop a coating on the cement grains. Furthermore, it initiates the development of ettringite and the dilution of Ordinary Portland cement. The initial and final setting time is quickened up with the increase (15–20 wt%) in MK content, which is attributed to the decline of water of consistency of cement mortar and filling effect caused by MK [19]. Badogiannise et al. [4] and Moulin et al. [40] reported dawdling in initial and final setting time in a range of 0–95% and 14–64%, respectively, when replaced with 20% of different types of MK. These remissions could be imputed to the fineness of different MK and the quantity and behavior of different plasticizers in each test.

3.3. Shrinkage

It is vital to slacken off the rate of shrinkage to maintain a durable structure since shrinkage initiates cracks in concrete. Guneyisi et al. [24] intensively studied the shrinkage properties of concrete. Shh et al. [57] conducted free shrinkage and restrained Shrinkage tests by incorporating SRA (shrinkage reducing admixture). The addition of SRA significantly declined the crack width of the restrained samples along with reduced free shrinkage. Kinuthia et al. [32] noted inflation in autogenous shrinkage of cement pastes at 5% and 10% replacement levels with MK. At the same time declination of autogenous shrinkage is observed at elevated replacement levels of 15% and 20%. Caldarone et al. [11] co-related the replacement of cement with 10% HRM to the shrinkage of concrete and thus 33% reduction in shrinkage was noted after 156 days. The test method for autogenous shrinkage was explained in detail in The Japan Concrete Institute 1988. Later on Brooks et al., [10] elaborated a most reliable method for the same and concluded that MK at higher replacement level dented the basic creep, drying creep, and the total creep of concrete.

3.4. Water/Binder ratio

The water/binder ratio influence the major parameters of concrete like compressive strength, pore size distribution, and capillary pores refinement. Concrete incorporated with MK is expected to refine the pore structure and limit permeability due to its filler effect. The chemically combined amount of water increases with elevated MK content up to 10% [60], which is attributed to the high specific surface area and the rise of water of consistency of cement paste. Furthermore permeability, porosity and sulfate attack found to decline at low w/b ratio [16]. More ettringite formation causes severe decay to concrete as well as more %wt loss caused by magnesium sulfate attack with the elevated w/b ratio [8]. Intense durability towards sulfate attack was observed in metakaolin concrete with a w/b ratio of 0.6, which developed more deterioration due to sulfate attack in a comparative study for MK concrete for a duration of 18 months [2]. Thus the permeability and porosity tend to decrease at low w/b ratio, which in turn lowers the sulfate attack minimizing the intrusion of sulfate ions. However, optimum w/b ratio for highest compressive strength was determined as 0.4 with 10% replacement level of MK [17]. The water-soluble (1.76 g/L at 10 °C) portlandite (CH), which is linked with the changes in relative strength, varies with the w/b ratio. The higher consumption of CH marks more formation of C–S–H, thus improving the strength of concrete. A w/b ratio of 0.5 is adopted for 30 and 40% metakaolin replacement when cured for 28 days in lime-saturated water for the complete removal of portlandite from the OPC [44]. Whereas another study reported 20% replacement of cement with MK is necessary to eradicate CH in a standard concrete at 28 days [33].

4. HARDENED CONCRETE

Strength, durability, and dimensional stability parameters are studied to replicate the hardened properties of concrete. Amidst compressive strength and tensile strength is the well-adapted common parameter for experimenting with the hardened concrete. Thermal and acoustic properties are considered under unique contingencies.

4.1. Compressive strength

The cardinal motif of introducing supplementary cementitious materials, fibers, and other admixtures are to enhance the compressive strength as well as to make the concrete economical by de-emphasizing the use of cement, which in succession taper off the CO_2 emission. Khatib et al. [29] limited the addition of MK up to 20% for which maximum refinement of pore structure and compressive strength is achieved, furthermore, the study concluded that beyond 30% the compressive strength decreases with the addition of MK. Wild et al. [59] suggested that irrespective of the replacement level of MK, the benefaction of MK in the intensification of concrete is restricted beyond 14 days. Whereas in silica fume it promotes strength enhancement at extended ages of at least 28% replacement levels [18].

For 15% of cement replacement similar strength development at 90 days and 180 days with MK and silica fume, respectively, were noticed, which can be related to the fineness of the micro-filler of MK specimens [14]. MK concrete under heat curing of 50 °C exhibits higher early strength at 7 days than the specimens which were cured at 20 °C. However, the enhancement of strength decelerates in the long term for 365 days [55]. Aishwarya et al. [1] analyzed the behavior of nano-metakaolin with concrete and concluded a higher increase in compressive strength for M20 grade concrete up to 37% compared with the other grades of concrete such as M30, M40, and M50.

4.2. Tensile strength

Development of strength for splitting tensile strength is rather a replica of compressive strength. For 20% wt of MK, the maximum tensile strength was observed for 0.35 and 0.55 w/b ratio in a comparative study [26]. Thus, splitting tensile strength was observed to increase along with the MK content in all ages. Compared to the compressive strength, the increase in split tensile strength was less. In another study, it was showcased that both split tensile strength and compressive strength are closely related. And technically both parameters are related to the strength of the concrete. It was also noted that the rise in tensile strength was low compared to that of compressive strength [43].

The variation in tensile strength was studied at 0, 5, 10, and 15% replacement of MK with cement. With the increasing MK replacement level, the tensile of concrete was found to increase mutually. Also, the bending strength showed high variations with a gain of 32 and 38% at 10 and 15% replacement, respectively [51]. In another study, the bending strength attained a maximum at 14 and 28 days in MK concrete [13]. The bonding strength capacity is found to increase by 35% when MK concrete is developed with steel fibers [25]. In another studies [6, 7] it was stated that by controlling the crack growth inside the concrete, the pull out resistance was enhanced when steel fibers were introduced.

4.3. Chloride resistivity

In order to determine the chloride resistivity of concrete, the electrical conductance of concrete is performed by allowing the chloride ions to penetrate into it. The resistance of chloride ions of concrete is directly proportional to the internal pore structure and permeability since highly permeable concrete allows a huge flow of current in it. For a period of 6 h, the amount of electrical current passing through in a 100 mm nominal diameter and 50 mm thick slice is monitored. A 60 V DC potential difference is maintained at both ends of the specimen, out of which one is immersed in sodium hydroxide solution and then other one in a solution of sodium chloride. The total amount of charge in coulombs is noted, which can be related to the resistivity of concrete specimens towards chloride ion penetration. This test is performed as per the [3]. Poon et al. [50] conducted rapid chloride diffusion test on specimens which were preheated to 600 and 800 °C since extreme damage occurs at high temperature and also to limit the long testing time of concrete. A high amount of charge is passed through indicating loss of impermeability at high temperatures. These results are accounted to the coarsening of the pore structure of concrete and internal cracking [12]. Nevertheless, concrete with 5% cement replacement for MK and SF performed better than the pure OPC because of the low CH content, which inhibits internal cracking when subjected to heating and disintegration on cooling [35]. An apparatus set up by McGrath [37] wasused in another study to experiment with the HRM [9].

4.4. Alkali silica reaction

The alkaline component in cement tends to react with the silica component in aggregate at suitable moisture conditions causing the formation of sodium silicate gel which is soluble and viscous in nature. The hygroscopic gel further starts swelling absorbing the water due to the expansive pressure, which in turn promotes spalling and strength loss of concrete. These reactions are often referred as “concrete cancer” and even promote demolition of the particular structure.

Incorporating 15% of MK in standard Portland cement completely eliminates the expansion of concrete caused by ASR, by limiting the freely available CH/SiO_2 (active) ratio and CH intercepting the swelling gel formation [33]. The C–S–H crystal obtained when MK reacts with the portlandite is much of a replica of the composition and structure of that of Portland cement [15]. Terrence et al. [52] conducted an extensive study on the ASR and found the alkali concentration of pore structure to be significantly low when 20% of MK is incorporated. For both moderate alkali cement and high alkali cement, the concentration of long term hydroxyl ion was lowered below 0.2 mol/L. They also concluded that the supplementary hydrates entrapped the alkalis as well as reduced the pH of pore solutions.

4.5. Fire resistance

It is mandatory to safeguard human life from fire accidents in structures as well as from structures (oil, gas, and power industries) which are exposed to elevated temperatures. An absolute analysis of each component of concrete is essential before introducing them in concrete structures for the better behavior of structures. Reduction of CH content, less permeability, dense pore structure, and constituent materials (pozzolans) alter the thermal behavior of concrete. For the complete elimination of CH, the amount required depends on Portland cement composition, curing condition, porosity of MK, and w/b ratio [44]. Reduced CH content develops high strength and durability to concrete even at a higher temperature [35]. Experimental analysis on MK concrete at high temperature was initiated by [50], in which the specimens were tested after 60 days. Specimens were heated up to 200, 400, 600 and 800 °C after 28 days water curing unstressed compressive strength test, permeability, resistance to chloride ion penetration, rapid chloride diffusion test, porosity, average pore size, and spalling frequency were tested after bringing down the specimen to room temperature. Compressive strength tends to increase at 200 °C followed by a sharp decline after 400 °C causing severe cracks and explosive spalling. Lower porosity and dense microstructure are responsible for the poor behavior of MK concrete at elevated temperatures. Due to the vapor pressure in dense pore structure, explosive spalling was observed between 450 and 500 °C. At all temperatures, MK concrete with 5% replacement performed better with no spalling. Morsy and El-Nouhy [39] analyzed the effect of high temperature on the physical–mechanical properties of MK mortar. In MK20 mix, a marginal gain of 1% is noted for compressive strength. In another study [38] by the same author, it was concluded that poor microstructure along with increased cracking and development of inappropriate configuration of C–S–H crystals are responsible for the strength loss in MK cement mortar. The sorptivity values increased with rise in temperature thus developing more resistance to penetration of water by capillary action [41].

4.6. Sulfate resistance

The intrusion of sulfate ions to concrete can cause severe damage by the weakening of the bond between cement paste and aggregate, extensive cracking and expansion. Reduced expansion of the mortar was noted with an increase in MK content (5–20%) when included in high and intermediate C_3A content cement [29]. At higher MK replacement levels, sulfate resistance of concrete was observed better. MK concrete with both 0.5 and 0.6 w/b ratio showed maximum sulfate expansion values of 0.4 and 0.45%, respectively for 10 and 15% MK replacement at 18 months [2]. In another study, MK concrete developed better chemical resistance than the PPC [54]. The resistance of MK concrete to sulfate attack was found higher at low w/b ratio, high air content (1.5–5%) and when autoclaved [2].

4.7. Pore structure and permeability

Cement mortar with metakaolin leads to refinement of the pore structure. High MK content increased the proportion of pores with radii less than 20 μm and also decreased the threshold value for paste [30]. Below 20% of MK content, the total porosity of cement mortar tends to decrease [60]. However, filler effect and increased w/b ratio caused high porosity beyond 30% of MK content along with decreased pore volume and threshold diameter [34]. The effect of MK on the pore size distribution of cement mortar is further detailed in another study. Total porosity was found to be about 16% more than the OPC paste along with pore size reduction, which can be attributed to the fineness of cement and MK used and also nature and composition [21].

4.8. Resistance to freezing and thawing cycles

A comparative study [31] was conducted for MK and SF when mixed with high strength concrete. Incorporating 5 and 10% of MK and SF, respectively, with 25% of w/b ratio on five mixtures, the freezing and thawing characteristics were studied. The relative dynamic modulus of elasticity was observed to remain quasi-constant for all the 5 types of concrete up to 300 cycles, which are attributed to the lower w/b ratio of entrained air content and HPC. This study thus depicts the resistance of MK concrete to freezing and thawing when compared with SF. In another case [22], when under three-point loading, freeze-thaw resistance of the specimens are studied. MK showed improved durability than SF which is attributed to the refining of the pore structure.

4.9. Resistance to aggressive agricultural environment and sea water

The resistance of concrete towards aggressive solutions and seawater is a crucial factor since it can cause further spalling of concrete which provokes the reinforcement to get exposed to the corrosive environment triggering the damage to the structure. Denser concrete and increased concrete cover can usually limit the reactivity of concrete to aggressive solutions and environment. The resistance of concrete to ammonium sulfate and solution of lactic acid reciprocating an aggressive agricultural environment is studied. 10% of MK content minimized the damage caused by lactic acid and found to be more pozzolanic than SF which was less reactive in more aggressive ammonium sulfate solution [28]. Another study [36] concluded MK can be incorporated to improve the durability of concrete subjected to aggressive action of silage effluents containing organic acids. In addition to that mass loss of concrete is reduced by 30% with 15% MK replacement when exposed to silage effluent.

5. METAKAOLIN IN SPECIAL CONCRETE

The high pozzolanic nature of metakaolin makes it more suitable when involved with special concretes. It further enhances the required parameter to a higher extent. The filler effect and fineness nature of MK makes it more flexible and aids in improving the physical and mechanical properties. The white color of the metakaolin is further an upper hand which enables to use it for decorative purposes too, unlike other pozzolanic materials.

5.1. Metakaolin in self-compacting concrete

Being a durable and flowable concrete, self compacting concrete (SCC) plays a key role in the recent construction era. Though it does not need manual compaction, it shows no bleeding and segregation. With less time and manpower SCC always heads off the other types of concrete. The highly pozzolanic material, metakaolin, when introduced in SCC, resulted in much better consistency and durability.

Rahmat et al. [61] attempted a thoroughgoing study on SCC with metakaolin. Slump value being the vital factor for SCC, when metakaolin was introduced, the values ranged between 660 and 715 mm. The range of slump throws light on the practical feasibility of the same. Adequate stability (Stability Index = 0 or 1) can be achieved in SCC with MK, without the usage of VMA. Though the passing ability was ceased, no blockage effects were noted in the L-Box test. Maximum compressive strength was obtained at 14 days (up to 27%) with improvement in both early age strength as well as compressive strength, and almost the same results were replicated in the tensile strength. The low absorption value (less than 3% at 30 min) indicating good quality of concrete even at lower w/b ratio is consequential. In the long range, 10% replacement of MK is considered as optimal value for concrete in view of net comfort.

5.2. Metakaolin in high performance concrete

High performance concrete was usually adopted in special cases in which durability parameters are bounded under particular environmental and structural requirements. Patil and Kumbhar [48] experimented on HPC with high reactivity MK and optimized 7.5% of the replacement for high compressive strength, after which the same seem to decline due to the decrease in w/b ratio and delayed pozzolanic activity. The chloride attack and sulfate attack resistivity were also enhanced for HPC with MK. Eva et al. [58] extensively studied the Czech MK in HPC and highlighted 10% of replacement as effective range for which excellent durability properties and chloride binding capacity were observed, while [23] optimized 8–12% replacement level for the improved durability performance and 15–20% replacement level for minimizing the expansion caused by ASR. Further, the increase in compressive strength was higher when high performance metakaolin concrete were developed with glass fibers of 12 mm length and 14 μm diameter [53].

6. CONCLUSION

With the aerial perspective from the literatures studied, a few conclusions were acquired as follows:

- The high specific surface and reactivity of MK lowers the workability
- 10% of replacement of MK with 0.4 w/b ratio developed maximum compressive strength
- The finer nature of MK lowers the porosity and thus a much permeable concrete is developed, which in turn provides resistance to chloride attack, sulfate attack, and acid attack
- The less CH content in the MK concrete tends to introduce high strength and durability to withstand the elevated temperatures
- Good gain in compressive strength was noted in MK concrete for up to a replacement level of 20% along with the inflation in tensile strength, which is comparatively lower than the former one
- Workability gets affected at higher MK replacement levels

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