Recent trend: Use of metakaolin as admixture: A review

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Abstract: Due to worldwide infrastructural development, since 20th century use of concrete has tremendously increased which resulted in heavy manufacturing of cement. Production of cement results in heavy environmental pollution due to emission of CO₂ gas. Also the raw materials used for the manufacturing of cement are quarried from the natural geological formations. Researchers have started working on partial supplementation of ordinary portland cement mineral or raw materials by naturally occurring, manufactured, or manmade waste. Various types of pozzolanic materials viz. fly ash, silica fume, metakaolin, blast furnace slag etc. are available which has cementous properties. Blending these materials with ordinary portland cement can improve the cementing and mechanical properties of cement. These days use of metakaolin is tremendously gaining popularity in partial replacement of cement due to its fineness in improving various strengths and parameters of mortars and concrete.

Key words: Pozzolanic materials, Ordinary Portland Cement, Kaolinite, Metakaolin, Mechanical properties

I. INTRODUCTION

Metakaolin is a dehydroxylated form of the clay mineral kaolinite. Rocks that are rich in kaolinite are known as china clay or kaolin, traditionally used in the manufacture of porcelain. The particle size of metakaolin is smaller than cement particles, but not as fine as silica fume. The quality and reactivity of metakaolin is strongly dependent of the characteristics of the raw material used. Metakaolin can be produced from a variety of primary and secondary sources containing kaolinite. Metakaolin is refined calcined kaolin clay under carefully controlled conditions to create an amorphous aluminosilicate which is reactive in concrete. Natural pozzolans like fly ash and silica, metakaolin also reacts with the calcium hydroxide (lime) byproducts produced during cement hydration. Between 100-200°C, clay minerals lose most of their adsorbed water. Between 500-800°C kaolinite becomes calcined by losing water through dehydroxilation. The dehydroxilation of kaolin to metakaolin is an endothermic process due to the large amount of energy required to remove the chemically bonded hydroxyl ions. Above this temperature range, kaolinite becomes metakaolin, with a two-dimensional order in crystal structure. This material is ground to a required fineness of 700-900m²/kg. In order to produce a pozzolan (supplementary cementing material) nearly complete dehydroxilation must be reached without overheating, i.e., thoroughly roasted but not burnt. This produces an amorphous, highly pozzolanic state, whereas overheating can cause sintering, to form the dead burnt, nonreactive refractory, called mullite.

The mineral composition of cement and metakaolin higly resembles with each other along with their functions. Table 1. Shows the major minerals in ordinary portland cement and metakaolin along with their functions as a binding material.

Table 1. Mineral Composition of Ordinary Portland Cement and Metakaolin.

<table>
<thead>
<tr>
<th>Major Minerals</th>
<th>Abbreviation</th>
<th>Percentage</th>
<th>Function of Minerals</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Cement</td>
<td>Metakaolin</td>
</tr>
<tr>
<td>Lime</td>
<td>Cao</td>
<td>60.2-66.3</td>
<td>2.00</td>
</tr>
<tr>
<td>Silica</td>
<td>SiO₂</td>
<td>18.6-23.4</td>
<td>51.52</td>
</tr>
<tr>
<td>Alumina</td>
<td>Al₂O₃</td>
<td>2.4-6.3</td>
<td>40.18</td>
</tr>
<tr>
<td>Iron oxide</td>
<td>Fe₂O₃</td>
<td>1.3-6.1</td>
<td>1.23</td>
</tr>
<tr>
<td>Magnesium Oxide</td>
<td>MgO</td>
<td>.6-4.8</td>
<td>0.12</td>
</tr>
<tr>
<td>Sodium Oxide</td>
<td>Na₂O</td>
<td>.05-1.2</td>
<td>0.08</td>
</tr>
<tr>
<td>Sulphpor</td>
<td>SO₃</td>
<td>1.7-4.6</td>
<td>0</td>
</tr>
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</table>
Percentages of minerals in Table 1 for cement and metakaolin are self explanatory and justify the replacement of ordinary portland cement by metakaolin for enhancing better performance of cement.

II. LITERATURE SURVEY

Several researchers have studied on various parameters by replacing the cement by metakaolin, which includes fineness, mineral composition, workability, various strengths of cement mortars and concrete, permeability, chloride permeability, resistance to chemical attack, sorptivity, durability, alkali aggregate reactivity etc.

The mechanical properties were studied in mortars and the microstructural development in pastes by X-ray diffraction, thermogravimetry analysis, mercury intrusion porosimetry and isothermal calorimetry. They showed that 45% of substitution by 30% of metakaolin and 15% of limestone gives better mechanical properties at 7 and 28 days than the 100% PC reference. Also proved that calcium carbonate reacts with alumina from the metakaolin, forming supplementary AFm phases and stabilizing ettringite. Using simple mass balance calculations derived from thermogravimetry results, we also present the thermodynamic simulation for the system, which agrees fairly well with the experimental observations. It is concluded that gypsum addition should be carefully balanced when using calcined clays because it considerably influences the early age strength by controlling the very rapid reaction of aluminates [1].

Studies on two parts, firstly the effectiveness of four minerals admixtures Viz. fly ash, silica fumes, high Reactive metakaolin, and black carbon with varying particle size gradations and shapes was investigated from a rebound reduction point of view. Secondly high reactive metakaolin and silica fume were compared on the basis of hardened mechanical properties with special emphasis on flexural toughness in presence of fiber reinforcement. They found that in rebound reduction particle size is more governing factor than its shape and silica fume is more superior than high reactive metakaolin due to its fine particle size but the blend of silica fume and high reactive metakaolin achieves overall better properties [2].

The effect on mechanical and durability properties of high strength concrete by incorporating metakaolin at a constant water/binder ratio of 0.5 was studied. Metakaolin mixtures with cement replacement of 5%, 10% and 15% were designed for target strength and slump of 90 MPa and 100 ± 25 mm. They observed that 10% replacement level was the optimum level in terms of compressive strength, beyond 10% replacement levels, the strength was decreased but remained higher than the control mixture. Compressive strength of 106 MPa was achieved at 10% replacement. Splitting tensile strength and elastic modulus values have also followed the same trend. In durability tests MK concretes have exhibited high resistance compared to control and the resistance increases as the MK percentage increases. This investigation has shown that the local metakaolin has the potential to produce high strength and high performance concretes [3].

Laboratory evaluations were carried out to assess the long term performance of concrete containing high reactive metakaolin produced in North America for resistance to chloride penetrations and reduction in expansion due to alkali silica reactivity. However, the reduction was not large enough to depassivate steel reinforcement [4].

Experiments on two metakaolins with similar mineralogical compositions but with different surface areas were carried out. Workability, setting time, strengths, elastic modulus, and heat evaluations were measured. It was observed that the effect of metakaolin surface area on compressive strength was particularly evident at lower water to cementitious materials ratios and generally at later ages. The greater surface area metakaolin caused a greater and more rapid heat evolution, indicating a higher reactivity and greater rate of hydration product formation [5].

The influence of low temperature on the performance of concrete containing metakaolin was studied by partial replacement of ordinary portland cement with 10 to 30% of metakaolin by weight of cement. The concrete was subjected to water and air curing at 5°C. Compressive strength was conducted on water cured specimen. They concluded that inclusion of 15% metakaolin increases linear shrinkage and beyond 20% metakaolin shrinkage is reduced [6].

Experimental study was carried out on the magnesium sulphate resistance of mortar and paste incorporating different percentages of metakaolin. Their results confirmed that mortars having high metakaolin showed lower resistance to sulphate concentrations of magnesium solution. However in lower metakaolin there were no visibly differences in the deterioration of mortars specimens. They concluded that it is necessary to pay special attention when metakaolin concrete is exposed to highly concentrated magnesium sulfate solution [7].

Researcher studied and described the strength enhancement observed in mortars containing metakaolin additions between 10 and 30%. It was found that compressive strengths increase with increased curing times and depended strongly on the activation temperature used. Strength enhancements did not depend significantly on the concentration of metakaolin addition. Significant improvements in compressive strengths of cement mortars, up to 80% or more, was found in selected cases [8].
Study on fresh concrete properties of high strength fibre reinforced concrete with metakaolin was done which included wet density, temperature and workability by addition of crimped steel fibres at 0%, 2.5%, 5%, 7.5% and 10% of weight of cement and metakaolin at 0%, 5%, 10%, 15% and 20% to the weight of cement. The fiber considered in this study was crimped steel fibre having aspect ratio 85. Experimental investigation was done using M60 mix with w/c ratio 0.3 [9].

Changes on some mechanical properties of concrete specimens produced by metakaolin, fly ash and steel fibers with the objective to obtain more ductile high strength concrete were observed. Three types of steel fibers were used in the experiments and volume fractions of steel fiber were 0.5% to 4.0%. The mechanical strength as well as ductility was increased due to partial replacement of Metakaolin and steel fibres. The use of metakaolin increased mechanical strength of concrete. On the other hand, the addition of steel fiber into concrete improves ductility of high strength concrete significantly [10].

Replacement of cement with metakaolin was done to find out the durability of concrete against sulphate attack. Three replacements of cement with metakaolin (5, 10 and 15% by weight) were done with water cement ratio of 0.5 and 0.6. After the specified days, the samples were immersed in 5% sodium sulphate solution for 18 months. Metakaolin addition proved to be beneficial in improving the resistance of concrete to sulphate attack. Metakaolin with the water cement ratio of 0.5 exhibited better results in sulphate resistance than 0.6. Autoclaved cured specimens had better resistance against sulphate than moist cured specimens [11].

The effect of Metakaolin and silica fume on the properties of concrete was studied. Experimentation with seven concrete mixtures of 0, 5, 10, and 15% by mass replacement of cement with high reactivity metakaolin or silica fume, at a water cement ratio of 0.35 and sand-to-aggregate ratio of 40% was carried out. The effect of metakaolin or silica fume on the workability, strength, shrinkage and resistance to chloride penetration of concrete were also investigated. The incorporation of both metakaolin and Silica fume in concrete was found to reduce the free drying shrinkage and restrained shrinkage cracking width. It was also reported that the incorporation of metakaolin or silica fume in concrete can reduce the chloride diffusion rate significantly. The performance of silica fume was found to be better than metakaolin [12].

Eight mix proportions were used to produce high-performance concrete, where they replaced either cement or sand by 10% or 20% metakaolin by weight of the cement content. The strength development of metakaolin concrete was evaluated using the efficiency factor (k value). With regard to strength development the poor Greek metakaolin and commercially obtained metakaolin yielded the same results. The replacement with cement gave better results than that of sand. When Metakaolin replaced cement, its positive effect on concrete strength generally started after 2 days where as in case of sand it started only after 90 days. Both Metakaolin exhibited very high k-values (close to 3.0 at 28 days) and are characterized as highly reactive pozzolanic materials that can lead to concrete production with excellent performance [13].

Statistical models for predicting the consistency of concrete incorporating portland cement, fly ash and metakaolin were studied. From the experimental results of standard consistency tests, the effect of variations of pozzolanic replacement materials was obtained. Cement was replaced by 40% and 50%. Consistency parameters were found out from the best fit models. Values of consistency were calculated by the proposed models and gave a good agreement with observed experimental data. It indicated that the models were reliable, accurate and can be used in practice to predict the consistency of portland cement-fly ash-metakaolin blends [14].

Study of a set of parameters of high performance concrete (HPC) with metakaolin including physical characteristics, mechanical properties, fracture-mechanical properties, durability characteristics, hydraulic, thermal properties and chloride binding characteristics was carried out. Experimental results showed that the replacement of portland cement by 10% metakaolin as an optimal amount leads in most cases either to improvements or at least does not significantly impair substantial properties of the analyzed HPC. Basic physical properties and heat transport, and storage properties are very similar to common HPC, mechanical and fracture mechanical properties were improved, water- and water vapor transport parameters were substantially reduced, frost resistance was better, resistance against de-icing salts was found to be slightly worse but still meets very well the required criteria. They reported that the chemical resistance of concrete with 10% of metakaolin instead of portland cement in distilled water and HCl is better than for Portland cement concrete [15].

By partial replacement substance for cement in concrete, the use of metakaolin in concrete effectively enhanced the strength properties. The optimum level of replacement was reported as 7.5%. The result showed that 7.5% of metakaolin increased the compressive strength of concrete by 14.2%, the split tensile strength by 7.9% and flexural strength by 9.3% [16].

The effect of metakaolin on strength and workability of concrete was investigated. Results showed that the use of metakaolin decreased the workability and to get the required slump, high range water reducing admixtures (HRWRA) were essential. HRWRA resulted in deflocculation of metakaolin particles and thus a
well dispersion of metakaolin particles were achieved. The work concluded that use of HRWRA was very essential in concrete containing fine particles like metakaolin to achieve well dispersion and better results [17].

Study on the effect of steel fiber content on the mechanical properties of Steel Fibre Concrete with metakaolin by using destructive test (DT) under compression testing machine as well as nondestructive test (NDT) by rebound hammer was performed. M20 grade concrete with volume fraction of the round crimped steel fiber with 1%, 2%, 3% & 4% increment and 5%, 10%, 15% & 20% of metakaolin as a replacement of cement with water/cement ratio was taken as 0.5. Total 18 cubes for above mentioned percentage of steel fiber with metakaolin were tested under compression and by rebound hammer, results were compared with conventional concrete [18].

HPC’s containing different mineral as well as chemical admixtures exhibits different properties in fresh as well as hardened states. Several factors determine these properties like: type of mineral as well as chemical admixture, type of aggregates, water-cement ratio, curing method etc. They reviewed test results on HPC with metakaolin, silica fume, with and without fibers (steel, glass, polypropylene) etc [19].

It was observed and concluded that construction material, consumes natural resources like lime, aggregates and water. In this content, an interest was made by civil engineers to replace the composite concrete material with industrial wastes, agricultural wastes, and waste glass. In this content, metakaolin was a pozzolanic material used in wide range in partial replacement of cement in concrete which was treated as economical and also due to its pozzolanic action increases strength and durability properties of concrete. In view a review was done in utilization of metakaolin in concrete as a partial replacement material to cement which has given excellent results [20].

Experiments on self compacting concrete were carried out. Studied on its mix proportioning and testing methods for flow characteristics which they found different from those of the ordinary concrete was done. Super plasticizer was used for enabling flow while keeping coarse aggregate in a viscous suspension. They attempted to study fresh and hardened properties of self compacting concrete using metakaolin as partial replacement of cement in different percentages in addition to filler. Modified Nan-su method has been used for design mix as the study was carried out for medium strength of concrete [21].

The effect of partial replacement of cement by metakaolin by various percentages viz 0%, 10%, 20%, and 30% on the properties of high performance concrete, when it is subjected to magnesium sulphate attack was studied. An aggregate binder ratio of 2 and different water binder ratios viz. 0.3, 0.35, 0.40 and 0.45 was used in this investigation. Concrete specimens of size 150 x 150 x 150mm were casted to find residual compressive strength and specimens of size 100 x 100 x 100mm were casted to find percentage weight loss; both the sizes of specimens were casted and cured as per IS specification. After 28 days water curing, the concrete specimens were kept immersed in 5% concentrated magnesium sulphate solution for 30, 60 and 90 days for observation. Before immersion, they were weighed accurately and after required days of immersion and observation, specimens were removed from magnesium sulphate media, weighed accurately and tested for their compressive strength; weight loss and hardness of concrete were studied. The various results which indicate the effect of replacement of cement by metakaolin on HPC are presented in this paper to draw useful conclusions. The results were compared with reference mix. Test results indicate that use of replacement of cement by metakaolin in HPC has improved performance of concrete up to 10% [22].

Inclusion of metakaolin increases the compressive, tensile, flexural and bend strength and modulus of elasticity of concrete considerably; however, the workability is slightly compromised. This paper presents the review of investigations carried out to find the suitability of metakaolin in production of concrete[23].

Kinetics of air moisture absorption on three samples of metakaolin under industrial and laboratory condition from enriched kaoline at 23°C was studied. Time intervals for enriching equilibrium were established i.e. equilibrium moisture contents at relative humidity of the air varying between 64% and 97%. A kinetic equation is put forward to describe the experimental data at constant relative humidity of the air Ψ, as well as a generalized equation for the rate of process, which takes into account the influence of relative humidity. It was found that unlike water soluble substances in case of metakaolin the entire process occurs basically as adsorption [24].

Investigation was made on the reaction between metakaolin Ca(OH)₂-water and flyash- Ca(OH)₂-water. They observed that in the initial period of curing metakaolin combined lime with a very high rate that indicated that the overall rate of the reaction taking place in early age of portland cement- metakaolin concretes and cement mortars was limited by the hydration of cement phases. At initial stage the reaction between fly ash – Ca(OH)₂ and water was at a moderate rate as compared to metakaolin – Ca(OH)₂-water. Their results justified the combined use of metakaolin – fly ash ash- Portland cement in concrete industry [25].

Experimental performance was studied on the magnesium sulfate resistance of mortar and paste specimens incorporating 0%, 5%, 10% and 15% metakaolin (MK). The resistance of mortar specimens was evaluated using visual examination, reduction in compressive strength and expansion measurements. Results confirmed that mortar specimens with a high replacement level of metakaolin showed lower resistance to a higher sulfate.
concentration of magnesium solution. However, in a lower concentration, there were no visibly remarkable differences in the deterioration of mortar specimens, even up to 360 days of exposure, regardless of replacement levels of metakaolin. The negative effect of metakaolin on the magnesium sulfate resistance is partially attributed to the formation of gypsum but not ettringite and thaumasite. In addition, the reduction of calcium hydroxide and the increase of secondary C–S–H in the cement matrix due to pozzolanic reaction of metakaolin provided an opportunity to lead to the conversion of primary and secondary C–S–H gel into the M–S–H gel. It is concluded that it is necessary to pay special attention when using metakaolin in concrete exposed to highly concentrated magnesium sulfate solution [26].

The resistance of mortar specimens incorporating 0%, 5%, 10%, 15%, 20%, 25% and 30% metakaolin to the magnesium chloride solution was determined. Results confirmed that specimens with high replacement level of metakaolin showed higher resistance to magnesium solution. He observed that with the reduction of calcium hydroxide and the increase of secondary C–S–H in the cement matrix, metakaolin provide a good resistive agent to aggressive chloride solution by consuming liberated lime and so prevent the formation of Friedel’s salt. The maximum development of compressive strength was achieved for the specimens made from ordinary portland cement-metakaolin blended cement mortars containing a metakaolin content of 25% by weight. Bulk densities of all metakaolin mortar specimens were found between 1.4-2 gm/cm³ [27].

Mechanical properties of plain and metakaolin concretes with and without steel fiber were experimented. To develop the metakaolin included steel fiber reinforced concrete mixtures, portland cement was partially replaced with MK as 10% by weight of the total binder content. Two types of hook ended steel fibers with length/aspect ratios of 60/80 and 30/40 were utilized to produce fiber reinforced concretes. Two series of concrete groups were designed with water to binder ratios (w/b) of 0.35 and 0.50. The effectiveness of metakaolin and different types of steel reinforcement on the compressive, flexural, splitting, and bonding strength of the concretes were investigated. All tests were conducted at the end of 28 days of curing period. Analyses of variance on the experimental results were carried out and the levels of the significance of the variables on the mechanical characteristics of the concretes were determined. Moreover, correlation between the measured parameters was carried out to better understand the interaction between mechanical properties of the concretes. Their results revealed that incorporation of MK and utilization of different types of steel fibers significantly affected the mechanical properties of the concretes, irrespective of w/b ratio [28].

Tests on square large-scale steel-fiber-reinforced high-strength concrete HSC columns under concentric compression loading were performed. The experimental program was mainly designed to examine the effect of the volumetric steel-fiber ratio on the behavior of reinforced HSC large-scale elements subjected to axial compression loading. The test program was also designed to examine the combined confinement effect of steel fibers and transverse steel reinforcement. Thus, the test variables studied herein are the steel-fiber volumetric ratio and the volumetric ratio, yield strength, and spacing of the transverse steel ties. The results show that adding discrete fibers to HSC mixtures in reinforced concrete columns not only prevents the premature spalling of the concrete cover but also increases the strength and ductility of the axially loaded reinforced member. This behavior was predicted by the proposed fiber-reinforced concrete stress-strain model, which takes into account most of the parameters that influence confinement effectiveness: the concrete strength; the spacing, yield strength, volumetric ratio and configuration of the transverse reinforcement; the distribution of the longitudinal reinforcement; and the diameter, length, shape, volumetric ratio, and frictional bond strength of the fibers. Predictions were found to be in good agreement with experimental results [29].

Durability properties of steel fiber reinforced ,metakaolin blended concrete, when it is exposed to certain types of chemicals were investigated. Metakaolin is a thermally structured, ultra fine pozzolona, which replaces industrial byproducts such as silica fume, fly ash, etc., An experimental investigation has been carried out to evaluate the durability in terms of chemical resistance and weight loss of steel fibre reinforced concrete with and without metakaolin for concrete of M20 grade. In this investigation an attempt is made with chemicals like H₂SO₄ and HCl. Crimped steel fibres with 60 as aspect ratio at 0, 0.5%, 1.0% and 1.5% of volume of concrete are used.The results show that the percentage of weight loss is reduced and compressive strength is increased in the case of steel fibre reinforced concrete and concrete containing 10% metakaolin replaced concrete when compared to the normal concrete. Also the less percentage weight loss is noticed in the case of HCl and severe in the case of H₂SO₄[30].

III. CONCLUSION
It can be concluded that the partial replacement of cement by metakaolin has a good influence on the strengths of the cement mortars and concrete. The mineral morphology of both cement and metakaolin being identical contributes as a better binding material. Following advantages can be derived by use of 10 to 15% metakaolin by weight of cement with optimum fiber content varying from 1 to 3% by weight of cement.
i) It increases strengths of all basic properties viz. compressive strengths, flexure strengths, split strengths, tensile strengths etc.

ii) It reduces efflorescence which occurs when calcium is transported by water to the surface where it combines with carbon dioxide from the atmosphere to make calcium carbonate, which precipitates on the surface as a white residue.

iii) It increases resistance to chemical attack, and reduces alkali silica reactivity.

iv) It enhances workability and finishing of concrete.

v) It reduces shrinkage due to particle packing.

vi) It can be used in formation of high performance, high strength, and lightweight concrete, precast and poured-mold concrete, fiber cement and ferrocement products, glass fiber reinforced concrete, Countertops, art sculptures, mortar and stucco etc.

REFERENCES


