Influence of Metakaolin on the Mechanical Properties of Concrete: A Review

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Abstract— Use supplementary cementitious material is need of civil industry, because supplementary cementitious material (SCM) becomes essential part of high performance & high strength concrete mix design. These materials may be industrial waste, naturally available, by-product or manufactured consuming less energy. Some of widely used supplementary materials are fly ash(FA), bagasse ash(BA),rise husk ash(RHA), silica fume, granulated blast furnace slag(GGBS), metakaolin(MK), etc. Metakaolin is obtained from calcination of kaolinite between 650° – 800°c. The kaolin is transformed to an amorphous phase which is metakaolin. It has been widely used as a pozzolanic material in mortar and concrete. This paper overview of work carried out on the use of metakaolin as a partial replacement to cement in mortar and concrete.

Keywords- Concrete, Metakaolin, kaoline.

I- INTRODUCTION

Metakaolin (MK) is a pozzolanic material. It is obtained by the calcination of kaolinitic clay at a temperature ranging between 500 °C and 80 0 °C. The raw material input in the manufacture of metakaolin ($Al_2Si_2O_7$) is kaolin. Metakaolin on reaction with $Ca(OH)_2$, produces CSH gel at ambient temperature and reacts with CH to produce alumina containing phases, including C4AH13, C2ASH8, and C3AH6

1.1 PROPERTIES OF METAKAOLIN
Metakaolin had 99.9% particles b16 μm with a mean particle size of about 3 μm (Table 1). The typical chemical composition (Ambroise et al., 1994) is given in (Table 2)

1.2 USE OF METAKAOLIN:
The usage of Metakaolin has been found out in following aspects of mortar and concrete:

1. High performance, high strength and light weight concrete.
2. Precast members
3. Glass fibers reinforce concrete (GFRC)
4. Ferro cement

1.3 ADVANTAGES OF METAKAOLIN:
1. Enhance compressive and flexural strength
2. Increase durability
3. Increase resistance to chemical attack
4. Reduce shrinkage
5. Reduce effect of alkali-silica reactivity (ASR)
6. Enhance workability and finishing of concrete
7. Improve colour and appearance

Table1:Physical properties of metakaolin (www.metakaolin.com)

Property	Value
Specific gravity	2.60
Bulk density (g/cm3)	0.3 to 0.4
Physical form	Powder
Color	Off-White
GE Brightness	79–82

Table 2: Chemical composition of metakaolin (Ambroise et al., 1994)

Contents	% By Mass
Sio_2	51.52
Al_2O_3	40.185
Fe_2O_3	1.23
Cao	2.0
Mgo	0.12
K_2O	0.53
SO_3	0.0
Tio_2	2.27
Na_2O	0.08
L.O.I.	2.01

II. REACTION MECHANISUM

Thermal activation of clay minerals between 600–900 °C by dehydroxylation leads to the breaking down or partial break down of the structure forming a transition phase with high reactivity (Ambroise et al.,1986; Sayanam et al.,1989). One such example is the production of metakaolin ($Al_2O_3.2SiO_2$) orAS_2 by the calcinations of clay or soils rich in kaolinite (Pera et al. 1998). The principal reaction is between$AS2$ and CH derived from cement hydration, in the presence of water. This reaction forms additional cementitious C-S-H gel, together with crystalline products, which include calcium aluminate hydrates and alumosilicate hydrates ($C2ASH8$, C_4AH_{13} and C_3AH_6). The crystalline products depend principally on the AS_2/CH ratio and reaction temperature (Murat, 1983; Wild et al., 1998; Kinuthia et al., 2000).

Hydration reaction depends upon the level of reactivity of MK, which in turn depends upon the processing conditions and purity of feed clay. Reactivity level of MK can be determined by the Chapelle test (Kostuch et al., 1993; Asbridge et al., 1994), and is expressed as consumption rate of CH per gram of pozzolans. The amount of CH in hardened concrete can be determined by thermogravimetric analysis (TG) and differential thermal analysis (DTA). Table 3 presents the comparison of reactivity level of MK with silica fume (SF) and fly ash (FA). The reactivity of pozzolans can also be assessed by chemical determination of unreacted pozzolan in hydrated PC-pozzolan pastes.

(Kostuch et al. (1993) reported that (i) CH was significantly reduced during time for all replacement levels (0, 10, and 20%); and (ii) 20% replacement of cement by MK was required to fully remove all the CH in concrete at 28 days. (Oriol and Pera (1995) reported that between 30 to 40% MK is required to remove all the CH in MK-PC paste at a water binder ratio of 0.5 when cured in lime-saturated water for 28 days. (Ambroise et al. (1994) showed that during the hydration period, CH was quickly consumed, the microstructure was rich in CSH and stratlingite (C_2ASH_8), and the pore size distribution was displaced toward smaller values. At up to 30% replacement, MK acted as an accelerating agent, the pore size distribution was displaced toward small values, and the CH content was considerably reduced.

Table 3: Pozzolanic activity of pozzolans (Asbridge et al.1994)

Pozzolan	SF	FA	MK
Reactivity (mg) Ca (OH)$_2$/g pozzolan	427	875	1050

2.1. TEMPERATURE EFFECT

Pozzolanic reaction of metakaolin could be promoted by microwave heating (Oriol and Pera, 1995). As heat is generated quickly inside the cementitious material, thermal acceleration of the reaction was more efficient, allowing both reduction of the necessary amount of metakaolin (15% instead of 30–40% in normal conditions) and of the water: cement ratio (0.4 instead of 0.5). These results are quite interesting for the development of fiber-reinforced cement composites, in which microwave heating allows the reduction of the curing period.

In comparison with PC mortar, MK–PC mortars showed an enhanced temperature rise (Bai and Wild, 2002). Rojas (2006) have exhibited the presence of CSH and the coexistence of metastable and stable phases in a MK/lime system cured at 60 °C for 60 months of hydration. The metastable phasewas assigned to stratlingite (C2ASH8) and probably to C4AH13. The stable phase was attributed to katoite, a hydrogarnet structured phase. XRD pattern confirmed the presence of stratlingite and katoite as main crystalline compounds.

Rojas and Sánchez de Rojas (2003) studied the kinetics of pozzolanic reaction in MK/lime binder as well as MK-blended cement at 60 °C. Results showed that the sequence and formation of the hydrated phases was different in both matrices cured at 60 °C. In an MK/lime matrix, C_2ASH_8, C_4AH_{13} and C_3ASH_6 (hydrogarnet) were the main hydrated phases; while in MK-blended cement, stratlingite (C_2ASH_8) as the sole hydrated phase issued from pozzolanic reaction.

2.2. ALKALINE ACTIVATION

The alkali activation of metakaolin is a way of producing high strength cementitious materials. Alkaline activation of metakaolin with concentrated NaOH solutions produced an amorphous material—a zeolitic precursor with excellent cementing properties in terms of mechanical strength (Palomo et al., 1999).When metakaolin activation was carried out with highly concentrated alkaline a solution in the presence of calcium hydroxide, the main reaction product was sodium aluminosilicate similar to the one obtained when metakaolin was activated in the absence of calcium hydroxide (Alonso and Palomo, 2001). CSH gel was formed as a secondary product. The rate of polymer formation was influenced by parameters such as curing temperature, alkali concentration, initial solids content, etc. When the activator concentration increased, a delay in polymer formation was noticed, whereas temperature

accelerated its formation. The ratio metakaolin/Ca (OH)2 did not influence the rate of aluminosilicate formation, but larger amounts were precipitated when the solids ratio increased. The rate constant for hydration reaction for the metakaolin (MK)/ lime mixture samples cured at 60 °C was 68 times greater than the rate constant at 20 °C for the curing period up to 9 days (Rojas and Cabrera, 2002). At 20 °C, the sequence of appearance of the hydrated phases was C–S–H, C2ASH8 and C4AH13 while, at 60 °C, the sequence was C–S–H, C2ASH8, C4AH13 and hydrogarnet (C3ASH6). There was no evidence of further C2ASH8 and C4AH13 transformation into hydrogarnet in the mixture studied for 123 days at 60 °C.

2.3. EFFECT OF DEHYDROXYLATION

Flash-calcination enables the dehydroxylation of powdered kaolin clay within several tenths of a second, where traditional soakcalcinations require minutes at least (Salvador, 1995). The pozzolanic properties of the metakaolin produced from two different kaolinites, using two different flash calciners increased with the dehydroxylation rate, and rapidly decreased at the occurrence of recrystallization for temperatures above 900 °C. Flash-calcined products revealed structural properties different from soak-calcined products. Processing flash-calcination in a temperature range with a sufficient residence time led to metakaolins with lime reactivity similar or better than the reactivity of standard metakaolin, obtained by soak-calcination.

Shvarzman et al. (2003) investigated the effect of heat treatment parameters on the dehydroxylation/ amorphization process of the kaolinite-based materials such as natural and artificial kaolin clays with different amounts of amorphous phase (metakaolin). At calcination temperature below 450 °C, kaolin showed relatively low level of the dehydroxylation degree, less than 0.18. In the range from 450 to 570 °C, the degree of dehydroxylation sharply increased to 0.95, and finally between 570 and 700 °C, the kaolinite was fully dehydroxylated. The dehydroxylation was accompanied by kaolinite amorphization, which affected the activity of additives.

Table 4: Workability of metakaolin concretes (Wild et al., 1996)

Metakaolin	Super Plasticizer	Slump	Compacting Factor
0	0	5	0.81
5	0.6	10	0.84
10	1.2	15	0.88
15	1.8	25	0.89
20	2.4	75	0.89
25	3.0	75	0.89
30	3.6	90	0.90

III. FRESH PROPERTIES OF MORTAR/CONCRETE

Fresh properties of concrete containing MK were reported by Wild et al. (1996) (Table 4). Reduction in the slump values and increase in the setting times of concrete with the inclusion of MK were reported by Brooks and Johari (2001) (Table 5). Fluidity of MK-blended cement became poorer than that of PC with the inclusion of MK into PC at the same dosage of superplasticizer and the same water/binder ratio (Li and Ding, 2003). Bai et al. (2003a) used neural networks to predict workability of concrete incorporating metakaolin (up to 15%) and 40% fly ash. The models were reliable and accurate and illustrated how neural networks can be used to predict the workability parameters of slump, compacting factor and Vebe time across a wide range of PC–FA–MK compositions.

Table 5: Workability, Setting Times of MK Concretes (Brooks and Johari, 2001)

Mix	Slump	Initial Setting Time	Final Setting Time
OPC	100	5	7.7
MK5	30	6.42	8.82
MK10	20	6.98	9.42
MK15	5	6.45	9.31

Badogiannis et al. (2005) reported the results of water demand and setting times of cements containing five metakaolins. The metakaolinite contents in metakaolins MK1, MK2, MK3, and MK4 (derived from poor Greek kaolins) were 36, 37, 71, and 49% but 95% in a commercial metakaolin (MKC) of high purity. The authors concluded that (i) blended cements demanded significantly more water than the relatively pure cement; and (ii) the initial and final setting time of metakaolin cements were affected by the metakaolin content. Cements with 10% metakaolin, generally, exhibited similar setting times to that of PC, while for 20% metakaolin content there was a delay in the setting. MK4 showed the greatest effect on the setting delay of the cements.

IV-PROPERTIES OF HARDENED MORTAR/CONCRETE

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4.1. PORE SIZE DISTRIBUTION

When MK content was below 20%, the total porosity of the paste decreased (Bredy et al., 1989). Beyond 30%, an increase in porosity was observed which could be attributed to the 'filler effect' of fine MK particles and also because of increasing w/b ratios with increasing metakaolin content. At 100 days of curing, the pore volume of mortar and the threshold diameter decreased in the presence of MK (Larbi and Bijen, 1992). Khatib and Wild (1996) determined the porosity and pore size distribution of cured OPC-metakaolin paste (Table 7). The incorporation of metakaolin in cement paste led to refinement of the pore structure. The threshold value for paste decreased with the increase in metakaolin content. The proportion of pores with radii smaller than 20 μm increased with the increase in metakaolin content. Total intruded pore volumes increased between the ages of 14 and 28 days for metakaolin paste.

Table 7: Pore volume and % of pores of pastes containing MK (Khatib and Wild, 1996)

Days	Pore Volume				% Of Small Pores (Radiib20 Mm)			
	Metakaolin (MK) (%)				Metakaolin (MK) (%)			
	0	5	10	15	0	5	10	15
3	262.0	257.6	284.1	277.6	22.2	28.3	31.0	39.9
7	229.6	261.7	268.8	251.6	26.5	32.1	41.0	50.4
14	209.9	203.4	221.0	212.1	30.3	43.0	53.9	55.7
28	189.1	205.3	237.1	222.7	33.7	43.5	48.7	54.9
90	181.4	180.8	219.6	198.9	37.3	44.7	49.9	57.6

4.2. WATER ABSORPTION AND SORPTIVITY

Khatib and Mangat (1995) exhibited that sorptivity values determined on concrete taken from the top surface of a concrete cube can be several times greater than those for concrete taken from the bottom surface of the cube. In addition, carbonation influenced sorptivity. Aircured concrete, over a 4-year period, underwent an increase in mass and a reduction in sorptivity as a result of carbonation of the surface zone (Dias, 2000). Courard et al. (2003) indicated that water absorption of concrete mixtures increased with the increase inMK content at 28 days and 14months (Table 8). Khatib and Clay (2004) reported the increase in water absorption (WA) of concrete mixtures with the increase in MK contents at all curing times. Similar observationswere alsomadeby (Razak et al., 2004)

Table 8: Water absorption for mortars with cement CEM I 42.5, metakaolin and kaolin (Courard et al., 2003)

Material	Water Absorption (% Mass)		Decrease Ratio
	After 28 Days	After 14 Months	
Cement	7.82	8.16	4.1
5% Metakaolin	8.39	8.04	4.1
10% Metakaolin	8.78	8.44	3.9
15% Metakaolin	9.71	8.77	9.7
20% Metakaolin	9.70	8.97	7.5
25% Metakaolin	9.51	7.90	16.9

4.3. COMPRESSIVE STRENGTH

Inclusion of MK as partial replacement of cement enhanced the compressive strength of concrete, but the optimum replacement level of OPC by MK to give maximum long term strength enhancement was about 20% (Wild et al., 1996). Brooks and Johari (2001) also reported that compressive strength increased with the increase in the metakaolin content similar results were also reported by Li and Ding (2003) where concrete achieved the best compressive strength with 10% MK content.

Cement pastes containing 5% to 20% MK had higher compressive strengths than the control at all ages from 3 to 90 days, with the paste containing 10% MK performing the best (Poon et al., 2001). Jin and Li (2003) concluded that (i) incorporation of metakaolin can prompt both the strength and modulus of elasticity development of a young concrete; and (iii) metakaolin showed the best enhancement on the mechanical properties of young concrete.

Poon et al. (2003) concluded that concrete containing MK (0 to 20%) showed a distinct pattern of strength gain and loss at elevated temperatures up to 800 °C. After an increase in compressive strength at 200 °C, the MK concrete suffered a more severe loss of compressive strength. A sharp reduction in compressive strength was observed for all HSC beyond 400 °C followed by severe cracking and explosive spalling. Within the range 400–800 °C, MK concretes suffered more loss and possessed lower residual strengths than the other concretes.

Badogiannis et al. (2004) investigated the effect of metakaolin on the compressive strength of concrete. Poor Greek kaolin (C) was thermally treated and the produced metakaolin (MK) was superfine ground. In addition, a commercial metakaolin (MKC) of high purity was used. In concrete mixtures, metakaolin replaced either cement or sand in percentages of 10% or 20% by weight of the control cement content. The strength development of metakaolin concrete was evaluated using the efficiency factor (k value). The efficiency factor K was defined as the ratio of the mass of cement to the mass of the metakaolin when they had equivalent effect on the water-to cement ratio. The produced metakaolin (MK) as well as the commercial one (MKC) imparted a similar behavior with respect to the concrete strength. Both metakaolins exhibited very high k-values (close to 3.0 at 28 days) and were characterized as highly reactive pozzolanic materials that can lead to concrete production with an excellent performance. When metakaolin replaced sand, higher strengths than the OPC concrete were obtained at all ages up to 90 days. When metakaolin replaced cement, its positive effect on concrete strength generally started after 2 days.

Badogiannis et al. (2005) studied the compressive strength o cement containing five metakaolins up to 180 days. The metakaolinite contents in metakaolins MK1, MK2, MK3, and MK4 (derived from poor Greek kaolins) were 36, 37, 71, and 49%, respectively, but 95% in a commercial metakaolin (MKC) of high purity. Metakaolin had a very positive effect on the cement strength after 2 days and specifically a 28 and 180 days. 10% metakaolin content seemed to be, generally, more favorable than 20%.

Razak and Wong (2005) presented a mathematical model for estimating compressive strength of high-strength concrete incorporating pozzolanic materials, based on the strength of a control ordinary Portland cement (OPC) concrete made with similar mixture characteristics and curing history. Accuracy of the model increased with concrete's age. At 28 days and above, 97% of the estimated strengths were within ±5% of the actual value.

Potgieter-Vermaak and Potgieter (2006) studied the compressive strength enhancement up to 28 days, in mortars containing metakaolin additions between 10 and 30%. Activation temperature of MK ranged from 550 to 850 °C for durations of 30 and 60 min. The best activation temperature to produce metakaolin from kaolin was N700 °C, and should preferably be at least 750 °C. The compressive strengths increased with increased curing times and depended strongly on the activation temperature used. Strength enhancements did not depend significantly on the concentration of metakaolin addition. Longer activation time yielded marginally higher compressive strengths in the mortars containing MK heated for 60min compared to material heated for 30 min.

4.4. TENSILE AND BENDING STRENGTH

Qian and Li (2001) investigated the tensile strength and bending strength of concrete incorporating 0, 5, 10, and 15% metakaolin as partial replacement of cement (Table 10). Tensile strength of concrete increased systematically with increasing metakaolin replacement. Metakaolin replacement of 5% had little effect on the bending strength of the concrete. At 10 and 15% replacement, the 28-day bending strength increased by 32% and 38%, respectively.

Courard et al. (2003) determined the effect of metakaolin additions on the bending strength ofmortar. Cementwas replaced on amass basis by 5–20% metakaolin (Fig. 6). Replacement of cement with metakaolin very marginally decreased the bending strength after 3 days and almost attained equal strength after 7 days. In contrast, mortar containing metakaolin attained higher strength after 14 and 28 days.

Table 9: Tensile and bending strength of concrete with different metakaolin replacement (Qian and Li, 2001)

MK content	(0%)	(5%)	(10%)	(15%)
Tensile strength (MPa)	3.35	3.58	3.88	4.29
Bending strength (MPa)	4.65	4.74	6.16	6.40

CONCLUSIONS

The use of by-products like fly ash, granulated blast furnace slag, silica fume, rice husk ash, and metakaolin in cement and concrete has gained significant importance because of the requirements of environmental protection and sustainable construction in the future. The use of metakaolin (MK) as partial replacement of cement in mortar and concrete has been extensively investigated in recent years. The literature reviewed clearly demonstrates that MK is an effective pozzolan.

1. MK helps in enhancing the early age mechanical properties as well as long-term strength properties of cement paste/mortar/concrete.
2. The partial replacement of cement with MK reduces the water penetration into concrete by capillary action.
3. Incorporation of metakaolin, as a partial cement replacement, into OPC pastes causes substantial changes in the chemical composition of the pore solution phase of the hydrated material.
4. MK modifies the pore structure of the cement, mortar, and concrete, and significantly reduces the permeability resulting in resistance of transportation of water and diffusion of harmful ions which led to the deterioration of the matrix.
5. Metakaolin replacement of cement is effective in improving the resistance of concrete to sulfate attack. The sulfate resistance of MK concrete increased with increasing the MK replacement level. Concrete containing 10% and 15% MK replacements showed excellent durability to sulfate attack.
6. Substitution of MK has shown to increase the chemical resistance of such mortars over those made with plain Portland cement. Mortars were relatively little affected by 1% hydrochloric acid,1% sulfuric acid, and 1% nitric acid environments, but those mortars made from all three series showed poor resistance to higher acid concentrations: 5% sulfuric acid, 5% acetic acid, and 5% phosphoric acid environments.
7. Incorporation of high reactivity metakaolin as a partial cement replacement between 10% and 15% may be sufficient to control deleterious expansion due to alkali-silica reaction in concrete, depending on the nature of the aggregate.

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