Chapter 4
Metakaolin

4.1 Introduction

Metakaolin (MK) is a pozzolanic material. It is a dehydroxylated form of the clay mineral kaolinite. It is obtained by calcination of kaolinitic clay at a temperature between 500°C and 800°C. Between 100 and 200°C, clay minerals lose most of their adsorbed water. Between 500 and 800°C kaolinite becomes calcined by losing water through dehydroxilization. The raw material input in the manufacture of metakaolin ($Al_2Si_2O_7$) is kaolin clay. Kaolin is a fine, white, clay mineral that has been traditionally used in the manufacture of porcelain. Kaolinite is the mineralogical term that is applicable to kaolin clays. Kaolinite is defined as a common mineral, hydrated aluminum disilicate, the most common constituent of kaolin.

The dehydroxilization 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. In order to produce a pozzolan (supplementary cementing material) nearly complete dehydroxilization 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, non-reactive refractory, called mullite.

Metakaolin reacts with $Ca(OH)_2$, produces calcium silicate hydrate (CSH) gel at ambient temperature. Metakaolin also contains alumina that reacts with CH to produce additional alumina-containing phases, including C_4AH_{13}, C_2ASH_8, and C_3AH_6 [19, 71].

4.1.1 Uses of Metakaolin

Metakaolin finds its usage in many aspects of concrete:

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- High performance, high strength and lightweight concrete
- Precast concrete for architectural, civil, industrial, and structural purposes
- Fibre cement and ferrocement products
- Glass fibre reinforced concrete
- Mortars, stuccos, repair material, pool plasters
- Improved finishability, color and appearance

4.1.2 Advantages of Using Metakaolin

- Enhanced workability
- Increased compressive strength
- Increased tensile and flexural strengths
- Increased durability
- Reduced permeability
- Increased resistance to chemical attack
- Reduction in alkali–silica reactivity (ASR)
- Reduced shrinkage due to particle packing
- Reduced potential for efflorescence

4.2 Properties of Metakaolin

4.2.1 Physical Properties

Metakaolin particles are extremely small with an average particle size of 3 μm. Its colour is off-white (Fig. 4.1). Some physical properties of metakaolin are given in Table 4.1. SEM picture of typical metakaolin sample is shown in Fig. 4.2 [21].

Fig. 4.1 Metakaolin

Table 4.1 Physical properties of metakaolin

Property	Poon et al. [49]	Al-Akhras et al. [1]	Tafraoui et al. [65]
Specific gravity	2.62	2.5	2.5
Average particle size (μm)		1.0	12
Fineness (m^2/kg)	12,680	12,000	15,000–30,000
Physical form			
Colour		White	

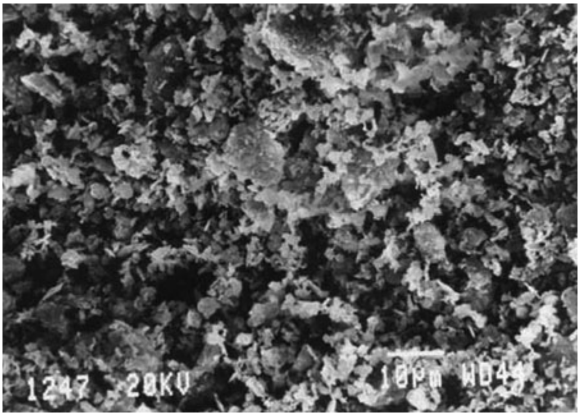


Fig. 4.2 SEM of metakaolin sample [21]

Janotka et al. [31] determined particle size distribution of Slovak poor metakaolin sands with different metakaolin content [36.0% (MK-1), 31.5% (MK-2) and 40.0% (MK-3]. The percentages of metakaolin sands were 10, 20 and 40%. Figure 4.3 shows the particle size distribution of metakaolin sands.

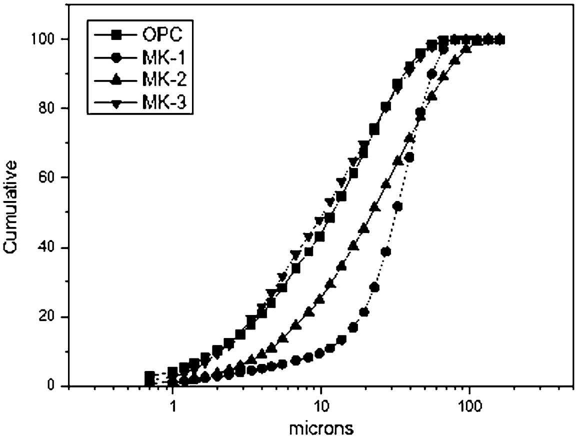


Fig. 4.3 Particle size distribution of Portland cement and metakaolin sands [31]

Table 4.2 Typical chemical composition of metakaolin

Ingredients (%)	Ambroise et al. [2]	Wild and Khatib [68]	Tafraoui et al. [65]
SiO_2	51.52	52.1	58.10
Al_2O_3	40.18	41.0	35.14
Fe_2O_3	1.23	4.32	1.21
CaO	2.00	0.07	1.15
MgO	0.12	0.19	0.20
K_2O	0.53	0.63	1.05
SO_3	–	–	0.03
TiO_2	2.27	0.81	–
Na_2O	0.08	0.26	0.07
L.O.I	2.01	0.60	1.85

4.2.2 Chemical Composition

Major constituents of metakaolin are silica oxide (SiO_2) and alumina oxide (Al_2O_3). Other components include ferric oxide, calcium oxide, magnesium oxide, potassium oxide, etc. The typical chemical composition of metakaolin is given in Table 4.2.

Metakaolin should meet the requirements of ASTM C618 [7], Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for use as a mineral admixture in Concrete, Class N, with the following modifications as given in Table 4.3.

4.2.3 Mineralogical Composition

Badogiannis et al. [8] reported mineralogical analysis of metakaolin produced from Poor Greek kaolin and commercial metakaolin (MKC). The semi-quantitative mineralogical estimation of MK and MKC are given in Table 4.4. The estimation is based on the characteristic X-ray diffraction peaks of each mineral, in combination with the bulk chemical analysis of the samples.

Table 4.3 Requirements of metakaolin (ASTM C 618)

Modified specification requirements

Item	Limit
Silicon dioxide (SiO_2) plus aluminum oxide (Al_2O_3) plus iron oxide (Fe_2O_3)	Min 85%
Available alkalies	Max 1.0%
Loss on ignition	Max 3.0%
Fineness: amount retained when wet-sieved on 45-μm sieve	Max 1.0%
Strength activity index at 7 days (% of control)	85
Increase of drying shrinkage of mortar bars at 28 days	Max 0.03%

Table 4.4 Mineralogical analysis of metakaolins [8]

	Kaolinite	Alunite	Quartz	Illite
MKC	96	–	–	3
MK	56	5	41	–

Table 4.5 Mineralogical phases of metakaolin sands [31]

Metakaolin sand	Metakaolin (wt.%)	Quartz (wt. %)	Illite (wt. %)	Albite feldspar (wt. %)	Muscovite (wt. %)
MK-1	36.00	21.85	6.93	4.23	31.00
MK-2	31.50	31.10	9.69	4.62	23.01
MK-3	40.00	18.11	6.18	3.82	31.90

Janotka et al. [31] reported the mineralogical phases (Table 4.5) of Slovak poor metakaolin sands with different metakaolin content. Contents of metakaolin varied between 31.50 and 40 wt. %, the rest was mainly sand.

4.3 Hydration Reaction

In Portland cement concrete, MK reacts at normal temperatures with calcium hydroxide in cement paste to form mainly calcium silicate hydrates (C–S–H), C_2ASH_8 (gehlenite hydrate), and C_4AH_{13} (tetracalcium aluminate hydrate). The formation of secondary C–S–H by this reaction reduces total porosity and refines the pore structure, improving the strength and impermeability of the cementitious matrix.

The optimum replacement percentage of cement with MK is associated with the changes in the nature and proportion of the different reaction products, temperature and reaction time. Hydration reaction depends upon the level of reactivity of MK in terms of the processing conditions and purity of feed clay. The feed clay (kaolin) should be either naturally pure or refined by standard mineral processing techniques; otherwise the impurities would act as diluents [41]. Reactivity level of MK can be determined by Chapelle test [4, 41]. Table 4.6 presents the comparison of reactivity level of MK with silica fume and fly ash. It is expressed as consumption rate of calcium hydrate per gram of pozzolans. The amount of CH in hardened concrete can be determined by thermogravimetric analysis (TG) and differential thermal analysis (DTA).

Kostuch et al. [41] observed that (1) CH was significantly reduced with age for all replacement levels (0, 10, and 20%); and (2) 20% by MK was required to fully

Table 4.6 Pozzolanic activity of various pozzolans [4]

Pozzolan	SF	FA	MK
Reactivity (mg) Ca $(OH)_2$/g pozzolan	427	875	1,050

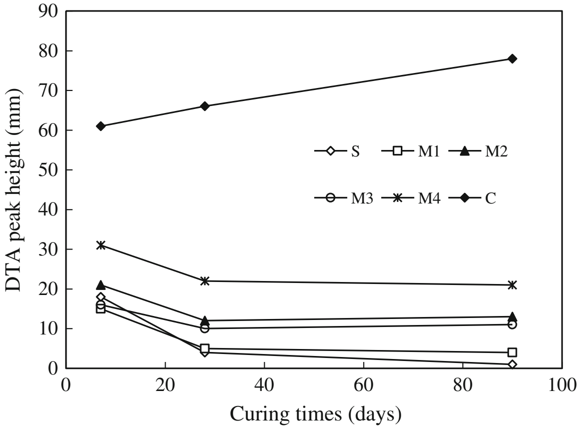
remove all the CH in concrete at 28 days where as Oriol and Pera [48] reported that between 30 and 40% MK is required to remove all the CH in MK-PC paste at a water-binder ratio of 0.5 when cured in lime-saturated water for 28 days.

Ambroise et al. [2] studied the early hydration period of pastes containing metakaolin using isothermal calorimetry and conductivity. Differential thermal analysis, X-ray diffraction, and Fourier transform infrared spectrometry were used to estimate the consumption of calcium hydroxide (CH) and identification of reaction products. The results showed that CH was quickly consumed, the microstructure was rich in CSH and stratlingite (C_2ASH_8), and the pore size distribution 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.

Curcio et al. [22] examined the role of metakaolin as pozzolanic micro-filler in high-performance mortars containing 15% metakaolin as replacement of cement. Water/binder ratio was 0.33. Four commercially available MK (M1, M2, M3, and M4) samples were used. Major chemical composition (SiO_2 and Al_2O_3) of M1, M2, M3, and M4 metakaolin were; 51.89 and 43.53%; 51.42 and 44.81%; 55.0 and 40.0%; 53.0 and 44.0%; respectively. Silica fume had 96% SiO_2. Figure 4.4 shows the height of the DTA peak of CH, occurring around 485°C, as a function of the curing time up to the age of 90 days. DTA calcium hydroxide peak heights on mortars and the pozzolanic activity test on mixtures of 80% cement and 20% microfiller showed that three of the four metakaolins had a remarkable pozzolanic activity comparable to that of silica fume, even if slightly lower at longer ages. The amount of CH changes very little after 28 days for the samples with metakaolins, slightly more for that with SF. MK1,MK2, and MK3 have a remarkable pozzolanic activity, comparable to that of SF, even if slightly lower at longer ages.

Klimesch and Ray [40] studied the effect of metakaolin on binding material and physical properties of cement–quartz pastes autoclaved at 180°C. Control cement–quartz mixture was prepared using 61.5% OPC and 38.5% quartz with the bulk C/S molar ratio (0.83) equivalent to that of $C_5S_6H_5$. MK contents were 6, 12, 18.25, 24,

Fig. 4.4 DTA $Ca(OH)_2$ peak height versus curing time [22]



and 30.5% as a quartz replacement in one series and as a cement replacement in another series. Water-to-total solids ratio of 0.46 was maintained in all mixtures. It was concluded that (1) for MK content up to 12%, the amount of tobermorite formation decreased when cement was partially replaced, whereas the opposite effect was observed in the case of partial replacement of quartz; (2) an overall reduction in compressive strength and drying shrinkage occurred with MK additions. In autoclaved systems, MK provided a source of silica that was more reactive than ground quartz; (3) when added as a quartz replacement, the amount of tobermorite decreased while hydrogarnet (C_3ASH_6) increased with the increase in MK content, indicating that hydrogarnet may prevail upon tobermorite by competing with it for Al_2O_3 and possibly SiO_2. However, when MK was used as a cement replacement, an increase in the tobermorite content was observed up to 12% addition followed by a sharp decrease at greater addition; and (4) MK addition, as either quartz or a cement replacement, also indicated that un-reacted MK will be present if the bulk Ca/Al molar ratio is less than 3. The decrease in these physical properties can be attributed mainly to increasing amounts of both hydrogarnet and α-C_2SH, and a general decrease in the C–S–H type binding phases.

Frías and Cabrera [24] studied the hydration rate of cement pastes containing 0, 10, 15, 20 and 25% of MK as partial replacement of cement. The water/binder ratio was 0.55 by weight. To determine the degree of hydration, it is necessary to know the total amount of calcium present in the hydrated MK/OPC systems. The total calcium hydroxide was calculated taking into account the weight loss due to the dehydroxylation of $Ca(OH)_2$ and the decomposition of $CaCO_3$. Figure 4.5 shows the percentage of calcium hydroxide with the curing time up to 360 days. It was observed that (1) calcium hydroxide contents of MK/OPC samples increased with age until 3 ± 7 days. Subsequently, the values start decreasing, more or less depending on MK content; (2) in 10 and 15% of MK mixtures, an inflexion point at 56 and 90 days, respectively was observed. Beyond this point, the calcium

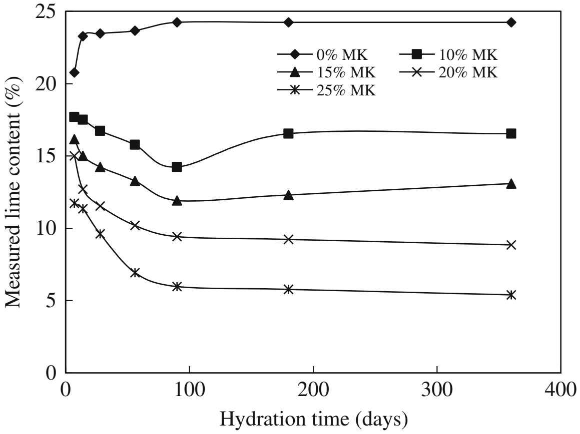


Fig. 4.5 Evolution of calcium hydroxide with time [24]

hydroxide content achieved a progressive increase. This behavior of calcium hydroxide content was due to different hydration mechanisms: the increase in the $Ca(OH)_2$ amounts are due to the OPC hydration, while the decrease in the values is related with the pozzolanic reaction of MK. The inflexion points (for 10 and 15% of MK) represent the end of the pozzolanic reaction, due to the total consumption of MK.

Sha and Pereira [62] investigated the hydration and pozzolanic reactions in cement pastes containing metakaolin (MK) as partial replacement of cement using differential scanning calorimetry (DSC) and thermal analysis. 100-mm cement paste cubes were made at water–solid ratio of 0.45 with 20 or 30% MK. The peak temperature and enthalpy are given in Table 4.7. They observed that pozzolanic effect of metakaolin even at this very early stage of hydration. The amount of calcium hydroxide drops by 25% when MK content increased from 20 to 30%. With this increase in MK content, the amount of OPC dropped by 14%. Also the crystallization peak increased by 24%, much less than expected from the 50% increase of the amount of MK.

Cabrera and Rojas [15] studied the reaction kinetics of a mixture of metakaolin and lime in water at 60°C using thermal analysis. Nature and quantity of the reaction products were determined by differential thermal analysis thermogravimetry and X-ray diffraction Based on the experimentation, they concluded that: (1) microwave drying to stop the hydration process was found to be a very practical and useful method that does not alter the nature of the reaction products. A drying time of 9 min was found to be adequate to drive off the free water from the metakaolin–lime–water mixture; (2) lime was consumed at a very rapid rate in the initial period of reaction (up to 50 h). The reaction mechanism was consistent with diffusion control for the first 120 h; (3) the reaction products detected from 2 h up to 9 days indicated that C_2ASH_8 and C_4AH_{13} phases were meta-stable for up to 9 days at 60°C under the circumstances studied, notwithstanding the fact that hydrogarnet (C_3ASH_6) was also present from 30 h up to 9 days. This might be an indication that hydrogarnet is not formed from a transformation reaction, but results from direct reaction between metakaolin and lime.

Table 4.7 DSC peak temperatures and enthalpy in constant heating runs for samples hydrated for 24 h in air in DSC [62]

Peak	Metakaolin (20%)		Metakaolin (30%)	
	T (°C)	J/g	T (°C)	J/g
C–S–H	118	–	120	–
Fe ettringite	No peak	–	177	0.4
Ettringite	No peak	–	198	0.9
C_4AH_{13}	No peak	–	291	1.2
Solid solutions	No peak	–	393	0.3
CH	455	40	482	30
$CaCO_3$	705	24	737	1.8
Crystallisation	935	42	968	52

Frías and Cabrera [26] examined metakaolin/lime and MK-blended cement pastes samples stored and cured at 20°C and up to 360 days of hydration. The nature of the reaction products and their sequence of appearance were obtained from differential thermal analysis and X-ray diffraction techniques. The results showed a different behavior of the pozzolanic reaction in both pastes. XRD data revealed the absence of crystalline phases in MK-blended cements up to 360 days of curing. MK showed high pozzolanic activity, which provided the quick formation of CSH, C_2ASH_8 (stratlingite), and C_4AH_{13} in MK/lime systems. The CSH was detected at 2 days of hydration time, followed by C_2ASH_8 and C_4AH_{13}. These two phases were detected at the same time.

In an MK/cement system (up to 25% of MK), the development of the hydrated phases presented a different behavior to the MK/lime system. The C_2ASH_8 was detected between 3 and 7 days of curing and it depends on MK contents. Subsequently, the C_4AH_{13} was possibly formed between 180 and 360 days. This phase was only detected with high MK contents, mainly with 25% MK. Below 20% MK, this phase was not identified. In the XRD patterns, for the MK/lime systems, the C_2ASH_8 was only identified as a crystalline hydrated phase, but not the C_4AH_{13}. This fact indicated very low crystallinity of the C_4AH_{13} with respect to the C_2ASH_8 phase. In MK-blended cement, XRD showed that the C_2ASH_8 formed during the pozzolanic reaction is an amorphous compound and on prolonged hydration it was possible to identify a very weak peak with high MK contents. The pozzolanic reaction in a blended cement matrix is more complex that in an MK/lime matrix, because of the presence of different ions (CO_2^{2-}, SO_4^{2-}, alkalis, chlorides), which could alter the kinetics as well as the development and crystallinity of the hydrates phases. It was due to the changes in solubility and evolution of the concentrations of the majority compounds (CaO, Al_2O_3, and SiO_2). These findings indicated that there was no formation of the C_4AH_{13} up to 180 days and the formation of an amorphous $C_2ASH_{8.}$

Poon et al. [49] reported the degree of pozzolanic reactions of high-performance cement paste made with 5, 10, and 20% metakaolin. The results (Table 4.8) of the pozzolanic reaction of the pastes, presented as % value of the reacted pozzolan relative to the initial amount of the pozzolan in the paste. Based on the test results, it was concluded that (1) degree of pozzolanic reaction of MK at each age was higher at a replacement level of 5% than at the replacement levels of 10 and 20%. The higher rate of pozzolanic reaction in cement pastes with a lower replacement level can be attributed to the higher concentration of CH available for the pozzolan to react with; (1) at 3 days, the degree of pozzolanic reaction of MK in the pastes at 5 and 10% MK content was 20.6 and 15.3%, respectively. The higher initial

Table 4.8 Degree of reaction of blended cement pastes [49]

Mix	Degree of reaction of pozzolans (%)			
	3 days	7 days	28 days	90 days
5% MK	20.56	29.52	39.44	56.28
10% MK	15.34	26.98	36.28	50.96
20% MK	9.38	18.64	30.82	41.29

reactivity of MK can be attributed to its Al_2O_3 phases [22], which are involved in the formation of gehlenite (C_2ASH_8) and a small amount of crystalline C_4AH_{13} phase [47]; and (3) although the rate of MK reaction became slower after prolonged curing, there was still a considerable increase in the degree of pozzolanic reaction of MK from 28 to 90 days. For cement paste with 10% MK, the degree of pozzolanic reaction of MK was 36.3% at 28 days and 51.0% at 90 days. The reaction of MK was not completed at the age of 90 days and about half of the MK remained unreacted.

Sun et al. [64] studied the hydration process of K-PS geopolymer cement under an 80% RH environment using environmental scanning electron microscope (ESEM). The ESEM micrographs showed that metakaolin particles pack loosely at 10 min after mixing, resulting in the existence of many large voids. As hydration proceeded, a lot of gels were seen and gradually precipitated on the surfaces of these particles. At later stage, these particles were wrapped by thick gel layers and their interspaces were almost completely filled. The corresponding energy dispersive X-ray analysis (EDXA) results illustrated that the molar ratios of K/Al increased while Si/Al decreased with the development of hydration. As a result, the molar ratios of K/Al and Si/Al of hydration products at an age of 4 h amounted to 0.99 and 1.49, respectively, which were close to the theoretical values (K/Al = 1.0, Si/Al = 1.0 for K-PS geopolymer cement paste). In addition, well-developed crystals could not be found at any ages; instead, sponge like amorphous gels were always observed.

Badogiannis et al. [9] investigated the hydration rate of metakaolin pastes. The metakaolinite content in metakaolin (MK4, derived from poor Greek kaolins) was 49%, where as it was 95% in a commercial metakaolin (MKC) of high purity. Cement was replaced with 0, 10, and 20% metakaolin. The weight loss up to 550°C, which corresponds to the total water incorporated in the cement paste (total combined water), was determined. The $Ca(OH)_2$ content, which for PC is directly related to the hydration of silicate compounds, was also measured. When pozzolanic materials were combined with PC, the $Ca(OH)_2$ content (when compared to that of PC alone) also provided an indication of the pozzolanic reaction. The weight loss in the range 600–700°C, if any, corresponds to the decomposition of $CaCO_3$ and it has to be converted to the equivalent $Ca(OH)_2$. The water combined in the hydration products (other than calcium hydroxide) corresponds to the weight loss up to 300°C. Any changes of this value indicated that the quantity, type and relative proportions of the hydration products are changing.

Figure 4.6 shows the calcium hydroxide content, total combined water and water in the hydration products at the age of 7 days. There was significant decrease in calcium hydroxide content in samples containing metakaolin in comparison to PC because of pozzolanic reaction. Also the pozzolanic reaction was more rapid in samples containing the commercial metakaolin MKC. This phenomenon is related to the higher fineness of MKC as well as to its higher metakaolinite content (95%). In contrast, pastes containing MK4 exhibited higher values of total combined water and water in the hydration products than the MKC pastes, probably due to the different hydration products.

Fig. 4.6 Calcium hydroxide, total combined water and water in the hydration products for a hydration age of 7 days [9]

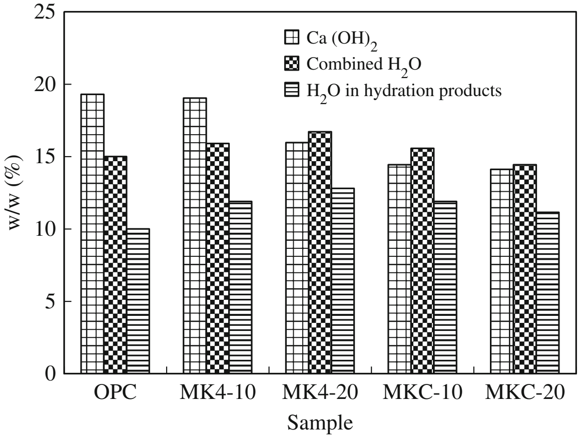
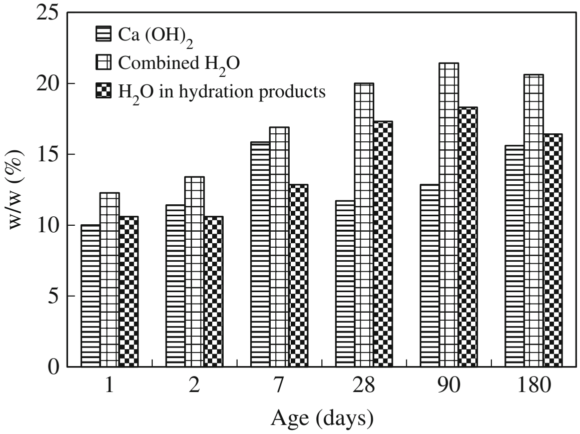


Figure 4.7 shows the calcium hydroxide content, total combined water and water in the hydration products for the sample MK4-20 in relation to the hydration age. A steep decrease of $Ca(OH)_2$ content was observed between 7 and 28 days, due to the acceleration of the pozzolanic reaction. At the same period, the change of the water combined in the hydration products (other than calcium hydroxide) could be attributed to the change of the quantity, type and relative proportions of the hydration products.

Wong and Razak [70] suggested an approach for the evaluation of efficiency factor (*k*) of a pozzolanic material. The cementing efficiency factor (*k*) of a pozzolan is defined as the number of parts of cement in a concrete mixture that could be replaced by one part of pozzolan without changing the property. The method, developed following Abram's strength—w/c ratio rule, calculates efficiency in terms of relative strength and cementitious materials content. The advantage of this method is that only two mixtures are required to determine the *k*-factor of a

Fig. 4.7 Calcium hydroxide, total compound water and water in the hydration products in relation to the hydration age for the sample MK4-20, 20% MK content [9]



specific mixture. A laboratory investigation on metakaolin (MK) concrete found that the computed efficiency factors varied with replacement level and age. At 28 days, the *k* values ranged from 1.6 to 2.3 for MK, while at 180 days, the k values varied from 1.8 to 4.0 for MK. Generally, the *k* factors increased with age but declined with higher pozzolanic content. It was also observed that change in w/cm ratio from 0.33 to 0.27 did not significantly affect the resultant efficiency factors. Based on the obtained results, it was concluded that a single *k* value for a pozzolan does not exist, even for specific cement–pozzolan content.

Kim et al. [38] studied the XRD patterns measured at 28 days for the ordinary Portland cement and the pastes mixed with 0, 5, 10, 15 and 20% of metakaolin. The XRD patterns of the hydrate products in pastes are presented in Fig. 4.8. It can be seen that the crystalline phase of CH (portlandite) decreases as the replacement ratio of MK and SF increases, while the weak peaks of C–A–H, in pastes replaced by MK, slightly increase. The decrease of the CH peak is related with the consumption by pozzolanic reaction of MK. Further EDS analysis revealed the

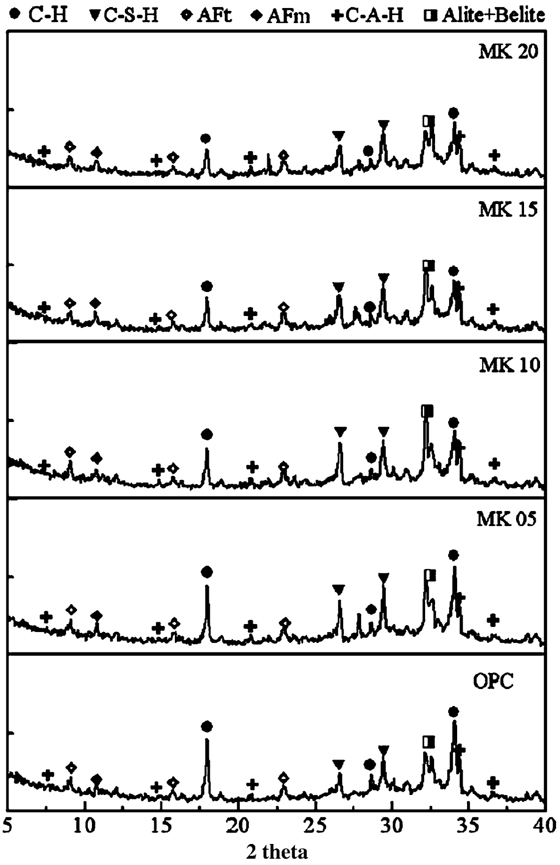


Fig. 4.8 XRD patterns of paste sample with replacement of metakaolin [38]

presence of C–S–H and CH as the main hydrated products in the case of ordinary Portland cement, and C–A–S–H and C–A–H were observed for MK paste.

Lagier and Kurtis [42] examined the influence of Portland cements of varying composition on early age reactions with metakaolin of varying surface area (11,100 and 254,000 m^2/kg). They observed that (1) metakaolins appeared to have a catalyzing effect on cement hydration, leading to an acceleration in the reaction rates, an increase in cumulative heat evolved during early hydration, and—for some cements—apparently an increased intensity in heat evolved during certain periods of early hydration. The surface area of the metakaolin also seemed to influence early hydration behaviour, with the higher surface area material producing a greater rate of heat evolution, greater cumulative heat, and greater intensities during early hydration; (2) strongly exothermic reactions appeared to occur between the cements and metakaolins, particularly in the first 24 h, and the reactions seemed to be most closely associated with the “third peak” observed in calorimetry—that which is most often related to the reaction of calcium aluminate phases; and (3) reaction of metakaolin appeared to be quite sensitive to variations in total alkali content in the cement.

Janotka et al. [31] investigated the hydration of cement paste containing Slovak poor metakaolin sands with different metakaolin content [36.0% (MK-1), 31.5 (MK-2) and 40.0% (MK-3)]. The percentage of metakaolin sands was 10, 20 and 40%. From the calorimetric results (Table 4.9), it was concluded that the addition of MK-1 and MK-2 sands to Portland cement induced a delay up to 2 h of the precipitation of the main hydration products in the blended-cement pastes and decreased the maximum heat evolution rate. On the contrary, the incorporation of 40% of MK-3 sand shortened 6 h its apparition and increased significantly the maximum heat evolution rate. The presence of the metakaolin sands reduced the heat released during the hydration process with respect to non-blended-cement pastes as a consequence of the precipitation of hydration products is less

Table 4.9 Calorimetric data for the Portland cement and metakaolin-blended-cement pastes [31]

Cement system	Peak start time (h)	Peak max. time (h)	Max. rate (J/g h)	Peak end time (h)	Peak duration (h)	Peak heat released (J/g)	Total heat released (J/g)
PC reference	1.87	12.98	9.15	96.86	94.99	272.03	310.12
PCMK-1/10	2.11	13.27	8.61	90.49	88.38	239.98	266.15
PCMK-1/20	2.15	12.98	8.17	114.54	112.39	249.25	296.68
PCMK-1/40	2.29	13.64	5.71	142.44	104.15	211.66	235.09
PCMK-2/10	2.09	13.91	7.84	91.01	88.92	241.77	245.07
PCMK-2/20	2.03	14.20	6.69	108.62	106.59	229.36	226.24
PCMK-2/40	2.22	15.32	4.56	121.17	118.95	168.80	171.28
PCMK-3/10	2.01	15.05	7.26	137.39	135.38	273.16	276.47
PCMK-3/20	2.07	13.07	13.07	123.25	121.18	269.51	273.44
PCMK-3/40	2.85	6.90	38.28	97.96	95.11	195.44	202.56

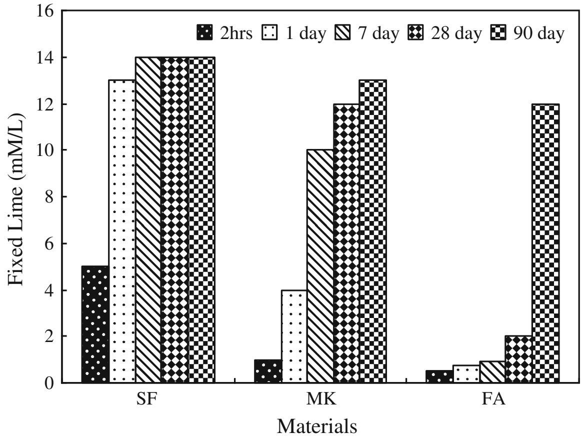
exothermic in the former and also the lower amount of hydration products formed in metakaolin sands-blended-cement systems.

4.3.1 Temperature Effect

Oriol and Pera [48] investigated the effect of a microwave curing on lime consumption in metakaolin blended cements. The microwave treatment conditions were assessed for plain Portland cement pastes, and then the lime consumption for various metakaolin contents was evaluated by Fourier transform infra-red (FTIR) spectrometry and differential thermal analysis (DTA). The results were compared with those obtained at room temperature. It was concluded that pozzolanic reaction of metakaolin could be consequently promoted by microwave heating. 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 (0.40 instead of 0.50).

Frías et al. [25] discussed the effect of metakaolin on the heat evolution in metakaolin–cement mortars in comparison to the behavior of other traditional pozzolanic materials such as fly ash and silica fume. The results revealed that MK mortars produced a slight increase in heating when compared to a 100% Portland cement mortar, due to the high pozzolanic activity of MK. With respect to the hydration heat, MK-blended mortar showed closer behavior to silica fume than to fly ash. The results obtained for pozzolanic activity are shown in Fig. 4.9. After 2 h, both the SF and MK showed pozzolanic activity, since the samples had fixed significant amounts of calcium ions (lime), while the FA, due to its lesser activity at early stages, hardly showed any reaction with lime before day 28.

Fig. 4.9 Variation of Pozzolanic activity: fixed lime over time [25]



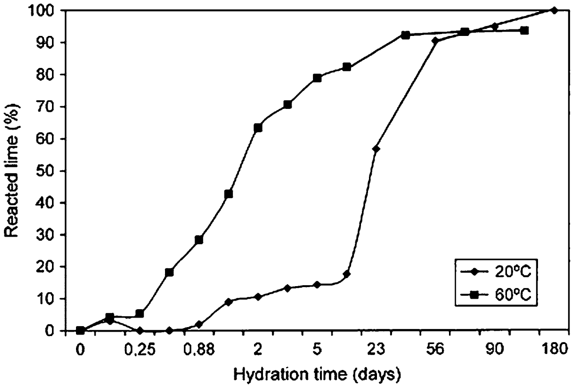


Fig. 4.10 Evolution of reacted lime with curing time at different temperatures [56]

Rojas [58] determined the effect of curing temperature on the reaction kinetics in a metakaolin/lime mixture cured at 60°C and after 60 months of hydration. The stability of hydrated phases formed during the pozzolanic reaction was evaluated. The results exhibited that metastable hexagonal phases (C_2ASH_8 and probably C_4AH_{13}) coexist with stable cubic phase (hydrogarnet) in the absence of lime. Also, there was evidence of the possible presence of a calcium aluminum silicate hydroxide hydrate (vertumnite). DTA curve showed 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 phase was assigned to stratlingite (C_2ASH_8) and probably to C_4AH_{13}. The stable phase was attributed to katoite, a hydrogarnet structured phase. XRD pattern confirmed the presence of stratlingite and katoite as main crystalline compounds present under tested conditions.

Rojas and Sánchez de Rojas [57] carried out an experimental study on kinetics of pozzolanic reaction in MK/lime binder as well as MK-blended cement at 60°C. The sequence, development and crystallinity of hydrated phases up to 123 days of curing time were studied by means of DTA and XRD techniques. It is well known that the pozzolanic reaction between metakaolin and calcium hydroxide produce CSH, stratlingite (C_2ASH_8), C_4AH_{13} and hydrogarnet (C_3ASH_6). However, the presence or absence of these hydrated phases depends on different parameters, such as curing temperature, matrix used, etc. They concluded that (1) the sequence and formation of the hydrated phases was different in both matrices cured at 60°C; (2) in MK/lime system (1:1 in weight), hydrated phases formed at high temperature were essentially CSH, C_2ASH_8, C_4AH_{13} and C_3ASH_6. CSH was detected at 6 h of hydration time, followed by C_2ASH_8 and C_4AH_{13} at 12 h of curing and finally C_3ASH_6 at 30 h of age; (3) in a MK-blended cement system (10, 20 and 25% of MK), the development of hydrated phases presented a different behavior from the MK/lime system. Stratlingite was detected in all cases as the sole reaction product from pozzolanic reaction. There was no evidence of formation of C_4AH_{13} and hydrogarnet (only traces); (4) XRD patterns for the MK/lime systems, stratlingite and hydrogarnet were identified as crystalline hydrated phases but not C_4AH_{13}; (5) in MK-blended cement at 60°C, XRD showed important changes with respect to the crystallinity of hydrated phases. Stralingite did not appear as a crystalline phase, indicating a very low crystallinity of this compound in blended cements. At 20 and 25% of MK, the presence of hydrogarnet traces was observed.

Rojas and Cabrera [56] studied the influence of curing temperature on the kinetics of reaction of a metakaolin ()/lime mixture. Chemical composition of MK was 51.5% of SiO_2, 41.3% of Al_2O_3, 4.64% of Fe_2O_3, 0.1% of CaO, 0.16% of MgO, 0.63% of alkalis and 0.83% of TiO_2. MK and analytical grade $Ca(OH)_2$ were mixed in a ratio of 1:1 by weight with a water/binder ratio of 2.37. Specimens were cured at 20 and 60°C. In the first case, the curing time varied from 2 h up to 180 days and, in the second case, from 2 h up to 123 days. A mathematical model was applied to calculate the rate constant for the hydration reaction. The amount of $Ca(OH)_2$ in cementitious materials can be measured quantitatively by thermal analysis. The results of lime consumption versus time are presented in Fig. 4.10. A different trend of decreasing lime content as the temperature increased was observed. In the samples cured at 60°C, lime was rapidly consumed during the first 120 h. Between 5 and 9 days, the amount of transformed lime at 60°C was approximately 65% higher than that at 20°C. Total lime consumption was 63, 82 and 92% at 2, 9 and 34 days, respectively. Beyond 34 days (between 34 and 123 days) of curing time, there is only an additional 1% of lime reacted. The curve corresponding to the samples cured at 20°C shows that lime is consumed at a slower rate than that at 60°C. The total consumption of lime was 10, 17 and 90% at 2, 9 and 56 days, respectively. However, at 180 days of curing time, lime had totally reacted by pozzolanic reaction. These results revealed an important increase in the activity of MK between 7 and 56 days at 20°C, while in the same samples cured at 60°C, the interval of maximum pozzolanic Activity was detected between 6 h and 2 days.

4.3.2 Effect of Dehydroxylation

Salvador [61] used flash-calcination processes to reduce the calcination time to a few seconds on fine products. Flash-calcination enables the dehydroxylation of powdered kaolinite clay within several tenths of a second, when traditional soak-calcinations require minutes at least. The pozzolanic properties of the metakaolin produced from two different kaolinites, using two different flash calciners increased with the dehydroxylation rate, and rapidly decreased occurrence of recrystallization for temperatures above 900°C. Flash-calcined products revealed structural properties different from soak-calcined products. Two different lime reactivity tests were done to asses the pozzolanic properties of products: the compressive strength and Chapelle test. Processing flash-calcination in a temperature range with a sufficient residence time, led to metakaolin with lime reactivity similar or better than reactivity of standard metakaolin obtained by soak-calcination. By measuring compressive strength, they verified that, after a flash-calcination, the quality of the pozzolana increased with α (degree of dehydroxylation) values. During the few seconds or tenths of seconds of flash-calcination, temperatures above 950°C induced recrystallization from the amorphous phase. Recrystallization was accompanied, as with a soak-calcination, by a rapid drop of lime reactivity. This performance drop was correlated with the decrease of the exothermic band surface area on DTA traces.

Shvarzman et al. [63] 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). The process of dehydroxylation/amorphization of kaolinite was characterized by DTA/TGA with mass-spectrometry and X-ray powder diffraction. Based on the study, they concluded that (1) at calcinations temperatures below 450°C, kaolin clays showed relatively low level of the dehydroxylation degree, less then 0.18. In the range from 450 to 570°C, the degree of dehydroxylation sharply increased to 0.95, and finally at the temperatures between 570 and 700°C the kaolinite was fully dehydroxylated since the only moderate change of degree of dehydroxylation was observed in this range (from 0.95 to 1.0); (2) the dehydroxylation was accompanied by kaolinite amorphization, which affected the activity of additives; (3) pastes containing less than 20% of amorphous phase can be considered as inert materials from the standpoint of pozzolanic activity. It was shown that chemical activity is a linear function of amorphous phase content (APC) in its range of 50–100%; (4) activity strength index (ASI) of mature mixes (7, 28 and 90 days) depends significantly on APC, as well as the degree of dehydroxylation. In contrast to the chemical activity, the increase of APC by over 55% did not lead to additional growth in ASI. Therefore, even with the partial dehydroxylation of kaolinite accompanied with $\sim$55% amorphization the material may be considered as very active pozzolanic admixture (according to ASTM 618).

4.4 Fresh Properties of Mortar/Concrete Containing Metakaolin

Caldarone et al. [18] observed that although the slump of concrete containing 10% MK was reduced from that of concrete with Portland cement only, the concrete containing MK required 25–35% less high-range water-reducers (HRWR) than equivalent SF mixtures. This reduction in HRWR demand resulted in the concrete containing MK having less sticky consistency and better finish.

Wild et al. [67] reported the results of workability tests of metakaolin concrete. Portland cement was partially replaced with 0, 5, 10, 15, 20, 25, and 30% metakaolin Control concrete mixture proportion was 1:2.3:3.4 with water–binder ratio (w/b) of 0.45. Workability results are given in Table 4.10.

Brooks and Johari [14] reported decrease in slump values and increase in both initial and final setting times with the increase in MK content in concrete with mixture proportion of 1:1.5:2.5 with w/b ratio of 0.28 (Table 4.11).

Table 4.10 Workability of metakaolin concretes [67]

Metakaolin (MK) (%)	Superplasticizer (%)	Slump (mm)	Compacting factor	Vebe time (s)
0	0	5	0.81	26
5	0.6	10	0.84	15
10	1.2	15	0.88	10
15	1.8	25	0.89	9
20	2.4	75	0.89	7
25	3.0	75	0.89	4
30	3.6	90	0.90	5

Table 4.11 Workability, setting times of MK concretes [14]

Concrete mixes	Slump (mm)	Initial setting time (h)	Final setting time (h)
OPC	100	5	7.7
MK5	30	6.42	8.82
MK10	20	6.98	9.42
MK15	5	6.45	9.31

Qian and Li [53] studied the dosage of superplasticizers on the slump of high-performance concrete made with 0, 5, 10, and 15% metakaolin as partial replacement of cement (Fig. 4.11). It was observed that (1) increase in SP content increased the slump; and (2) slump of the HPC decreased with the increase in MK content.

Li and Ding [45] investigated the consistency and setting times of Portland cement containing metakaolin and ultra-fine slag (S). Four series of pastes were made. Test results of water consistency and setting times are given in Table 4.12. It was observed that (1) standard consistency of cement paste was in the range of 26.3–29.1%. Mixture PO had the lowest water requirement, but MK blended cement M1 had the highest water requirement. After slag was mixed with MK blended cement, the water requirement of cement mixture S2 and S3 was reduced,

Fig. 4.11 Relationships of slump with metakaolin replacement [53]

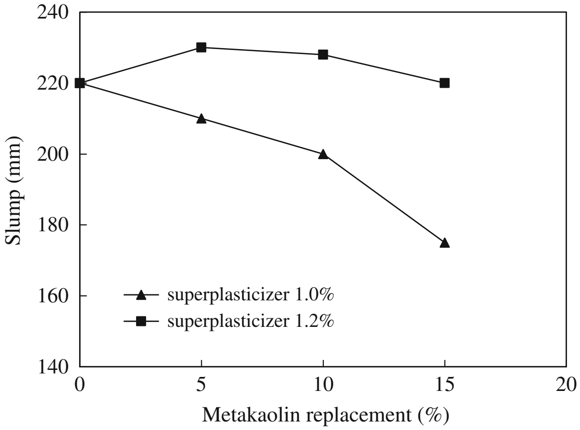


Table 4.12 Physical properties of cement paste [45]

Mixture type	Composition (%)			Water required for standard consistency (%)	Setting times (h:min)	
	Cement	MK	Slag		Initial	Final
PO	100	0	0	26.3	1:36	3:27
M1	90	10	0	29.1	1:11	2:12
S2	70	10	20	28.4	1:55	4:34
S3	60	10	30	28.0	2:19	6:15

Table 4.13 Physical properties of blended cements with metakaolin [11]

sample	Water demand	Setting time (min)	
		Initial	Final
PC	27.5	105	140
MK-10	32.5	155	180
MK-20	41.0	205	230
MKC-20	37.5	140	170

MKC commercial metakaolin with high purity, *MK* metakaolin produced from poor Greek Kaolin

but it was still higher than that of PC; (2) initial and final setting times of the cement incorporating 10% MK were shorter than those of PC, while the initial and final times of S2 and S3 cements were longer than those of PC.

Batis et al. [11] concluded that increase in metakaolin content increased the water demand and setting times of blended cements (Table 4.13). The blended cements demand significantly more water than the relatively pure cement and this phenomenon is attributed to the high fineness of metakaolin. The increase of the metakaolin content causes a significant increase of the water demand. PC with 10% MK (MK-10) showed the lowest water demand, compared with the other blended cements. The initial and final setting time of metakaolin cements is higher than the setting time of pure cement.

Badogiannis et al. [9] investigated the effects of five metakaolins (derived from poor Greek kaolins) and a commercial metakaolin (MKC) on the water demand and setting times of cements (Table 4.14). The metakaolinite contents in metakaolins (MK1, MK2, MK3, and MK4) were 36, 37, 71, and 49%, respectively. Commercial metakaolin (MKC) was of high purity (95% metakaolinite). Cement was replaced with 0, 10, and 20% metakaolin. It was concluded that (1) blended cements demanded significantly more water than the relatively pure cement. The increase in water demand could be attributed to the high fineness of metakaolin as well as to their narrow particle size distribution; and (2) the initial and final setting time of metakaolin cements was 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.

Kim et al. [38] investigated the effect of metakaolin (5, 10, and 15%) as partial replacement of cement on the flow rate of mortar. It was observed that flow values of mortar mixtures decreased with the increase in MK content. There was

Table 4.14 Properties of metakaolin cements [9]

Sample	Metakaolin (% w/w)	Water demand (% w/w)	Setting time (min)	
			Initial	Final
PC	–	27.5	105	140
MK1-10	10	29.0	75	130
MK2-10	10	29.0	85	130
MK3-10	10	32.0	105	160
MK4-10	10	32.5	155	180
MKC-10	10	31.0	95	130
MK1-20	20	32.0	105	160
MK2-20	20	31.5	110	165
MK3-20	20	38.5	120	160
MK4-20	20	41.0	205	230
MKC-20	20	37.5	140	170

approximately 8, 12, and 24% reduction in the flow value of mortars in comparison with that of the control mortar (0% MK) The results demonstrated the higher water demand with the increase in MK content.

Khatib [37] reported the workability of concrete containing metakaolin (MK) at a low water-to-binder ratio of 0.3. Portland cement (PC) was partially replaced with 0–20% MK. Results of slump, vebe time and compacting factor are given in Table 4.15. All mixes including the control (i.e. 0% MK) exhibited very low workability. Slump values were below 20 mm. Also Vebe times and compaction factors were more than 24 s and less than 0.8, respectively. The presence of MK reduces the workability.

Cachim et al. [17] examined the effect of metakaolin addition on the slump and density of hydraulic lime. Weight of hydraulic lime concrete ingredients were 1,074 kg coarse aggregates, 321 kg and, 550 kg of hydraulic lime, and 247.5 kg water. Two mixtures had a partial replacement of hydraulic lime by metakaolin. This replacement, by weight, was 20 and 30%. It was observed that slump values were 15, 8, and 16 mm for 0, 20 and 30% MK content whereas density of fresh concrete was 2,240, 2,220 and 2,160 kg/m^3.

Janotka et al. [31] investigated the effect of Slovak poor metakaolin sands with different metakaolin content [36.0% (MK-1), 31.5 (MK-2) and 40.0% (MK-3)] on the consistency and setting times of cement paste. The percentage of metakaolin sands in the blended cements was 10, 20 and 40%. Table 4.16 shows the consistency and initial and final setting times of Portland cement and metakaolin

Table 4.15 Workability of concrete mixes containing MK [37]

MK (%)	Slump (mm)	Vebe (s)	Compacting factor
0	17	24	0.87
5	12	25	0.86
7.5	8	27	0.83
12.5	3	30	0.81
15	2	36	0.80
20	0	37	0.78

Table 4.16 Properties of mortar containing metakaolin [31]

Cement system	Specific surface (m^2/kg)	Normal consistency	Setting times	
			Initial set	Final set
PC reference	428.27	29.6	3 h 25 min	4 h 40 min
PCMK-1/10	409.68	32.3	3 h 35 min	4 h 40 min
PCMK-1/20	415.97	38.0	3 h 50 min	4 h 55 min
PCMK-1/40	505.21	41.7	3 h 40 min	5 h 40 min
PCMK-2/10	401.58	30.2	3 h 25 min	4 h 30 min
PCMK-2/20	401.97	30.5	3 h 35 min	4 h 35 min
PCMK-2/40	375.91	32.5	4 h 10 min	5 h 40 min
PCMK-3/10	521.89	32.2	3 h 10 min	4 h 15 min
PCMK-3/20	605.21	36.2	3 h 05 min	4 h 05 min
PCMK-3/40	855.37	42.0	3 h 00 min	4 h 10 min

sand-blended-cement pastes. It was concluded that (1) normal consistency increased with the metakaolin content for all the three types; and (2) the incorporation of metakaolin sands MK-1 and MK-2 induced a delay of the setting times whereas MK-3 sand slightly accelerated setting times. This may be because of higher reactivity of PCMK-3 which is due to the higher specific surface and higher pozzolanic activity of MK-3 sand with respect to the other metakaolin sands.

4.5 Properties of Hardened Mortar/Concrete Containing Metakaolin

4.5.1 Pore Size Distribution

Bredy et al. [12] conducted study on porosity and pore size distribution of pastes containing MK. Pastes were made with MK content of 0–50% at different water-to-binder (w/b) ratios to maintain the same consistency. They concluded that total porosity of paste decreased when the MK content was less than 20%. Beyond 30%, an increase in porosity was found. Larbi and Bijen [43] reported that at 100 days of curing, inclusion of MK in mortar decreased pore volume and threshold diameter.

Khatib and Wild [34] reported the porosity and pore size distribution of OPC-metakaolin (0, 5, 10 and 15%) paste prepared at a constant water/binder (w/b) ratio of 0.55. The intruded pore volume and the pore structure were measured by mercury intrusion proximity. Pore volume of pastes containing metakaolin (MK) and proportion of pores with radii smaller than 20 µm are given in Table 4.17. For the control paste, there was a continuous reduction in total pore volume with age and also the rate of reduction declined with age. It can be seen from the table that total pore volume decreased with an increasing rate up to 14 days. Between 14 and 28 days, pore-volume increased. Beyond 28 days, pore volume again continued to decrease with age, but at a decreasing rate. This trend indicated that there was a

Table 4.17 Pore volume and % of pores of pastes containing MK [34]

Age (days)	Pore volume (mm^3/g)				Percentage of small pores (radii <20 μm)			
	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

clearly defined minimum point at around 14 days for pastes containing metakaolin. Also these pastes possessed a greater total pore volume than the control paste. Thus, the increase in pore volume between 14 and 28 days appeared to be associated with a renewed increase in CH content and a decline in relative strength. The proportion of pores with radii smaller than 20 μm was increased with the increase in metakaolin content.

Threshold value for paste decreased with the increase in metakaolin content. Figure 4.12 shows the threshold radius for pastes with and without metakaolin at different curing periods. The threshold radius is taken as the radius before which the cumulative pore volume rises sharply. Incorporation of metakaolin in cement paste led to refinement of the pore structure. The threshold value for paste decreased as the metakaolin content in the paste increased.

Ambroise et al. [2] determined the total porosity of blended cement with hydration time. Mortars mixtures (binder: sand = 1:3) were prepared: one with plain OPC, and the others with MK blended cements. The amounts of MK were 10, 20, and 30%, respectively. Total porosity of blended cements is given in Table 4.18. It was observed that porosity increased with the increase in MK content; (2) porosity is not proportional to the water demand: in spite of higher water demand (0.34 instead of 0.25), the blended cement containing 20% MK had nearly the same porosity as plain OPC, due to the efficiency of the pozzolanic reaction.

Frías and Cabrera [24] investigated the effect of hydration time (up to 360 days) on the average pore diameter of cement pastes containing 0, 10, 15, 20 and 25% of MK as partial replacement of cement. The water/binder was 0.55 by weight. To determine the degree of hydration, it is necessary to know the total amount of calcium present in the hydrated MK/OPC systems. Average pore size with hydration time is shown in Fig. 4.13. It was observed that (1) incorporation of MK reduced the pore size to less 100 Å. Gradual increase in the very fine pores was observed with age; (2) a strong reduction on the average pore diameter was observed in the first days. Depending on MK contents, the evolution of this parameter was different. In the case of OPC paste, the average pore diameter decreased from 40 to 14.5 μm for a hydration time between 1 and 56 days. Subsequently, the average pore diameter was almost a constant value. In paste with 10% of MK, the reduction of average pore diameter finished at 28 days while for

Fig. 4.12 Variation of threshold radius with age and varying MK content [34]

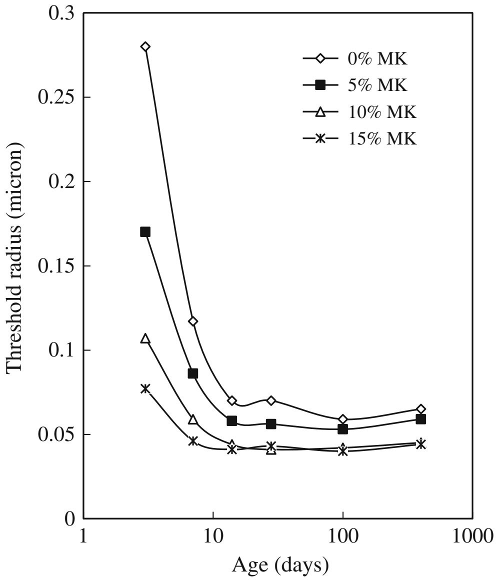
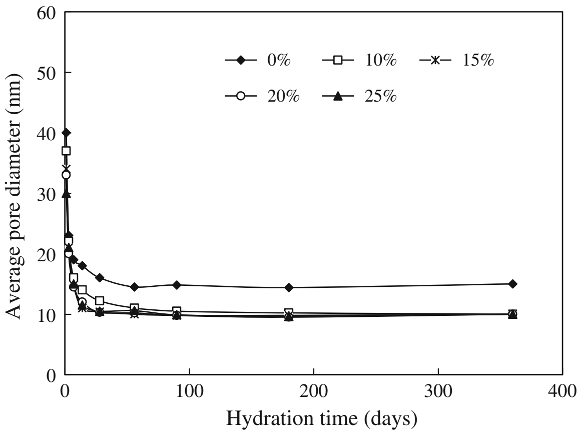


Table 4.18 Total porosity of MK blended cements (%) [2]

Mix No.	OPC: MK (%)	Water:solid ratio (W:S)	Curing time (days)			
			28	90	180	360
1	100:0	0.25	14.4	12.3	12.8	11.0
2	90:10	0.28	15.3	14.3	14.2	14.1
3	80:20	0.34	13.8	13.0	12.9	12.6
4	70:30	0.39	16.8	15.7	15.2	15.0
5	60:40	0.44	25.0	21.6	16.8	16.4
6	50:50	0.54	29.5	29.0	28.0	28.0

Fig. 4.13 Average pore diameter [24]



the 15, 20, and 25% MK pastes, this phenomenon occurred at 14 days. Above 10% of MK, the average pore diameter curves did not show any difference.

Poon et al. [49] investigated the porosity and pore size distribution of high-performance cement paste blended with metakaolin. The cement pastes were prepared with 5, 10, and 20% MK contents at w/b ratio of 0.3. Pore size and porosity were measured by Mercury Intrusion Porosemetry (MIP), and results are given in Table 4.19. Porosity and average pore size of pastes decreased with age. The pastes containing MK had lower porosity and smaller average pore diameters than the control paste.

Poon et al. [51] measured the total porosity of concrete mixes containing 5, 10, and 20% metakaolin as partial replacement of cement. Concrete mixes were made with w/b ratio of 0.3. The maximum nominal size of the coarse aggregate was 10 mm for the concrete with a w/b of 0.3, and 20 mm for the concrete with a w/b of 0.5. Porosity was measured with MIP, and results are given in Table 4.20. It was observed that the incorporation of MK in the cement pastes resulted in a very dense microstructure of the paste, with a lower total porosity in comparison with the plain Portland cement pastes

Badogiannis and Tsivilis [10] investigated the porosity of concretes made with Greek kaolin of low kaolinite content (49% metakaolinite, 72.1% SiO_2, 30% active SiO_2) and commercial metakaolin (95% metakaolinite, 54.6% SiO_2, 53% active SiO_2) of high purity. Concrete mixtures were made in which metakaolin replaced either cement or sand in percentages 10 or 20% by weight of cement.

Table 4.19 Average pore diameter and total porosity of blended cement pastes [49]

Mix	Average pore diameter (μm)			
	3 days	7 days	28 days	90 days
Control	0.0380	0.0371	0.0362	0.0348
5% MK	0.0357	0.0279	0.0257	0.0243
10% MK	0.0287	0.0251	0.0197	0.0186
20% MK	0.0204	0.0143	0.0122	0.0114
Total porosity of blended cement pastes				
Control	20.11	17.99	15.58	14.04
5% MK	18.17	15.36	13.82	12.51
10% MK	16.84	15.18	12.37	11.68
20% MK	16.30	12.85	10.73	9.21

Table 4.20 Total porosity of concrete mixes with w/b ratio of 0.3 [51]

Mix	MIP measured porosity (% v/v)			
	3 days	7 days	28 days	90 days
Control	8.69 ± 0.11	8.44 ± 0.13	7.92 ± 0.12	6.97 ± 0.28
5% MK	7.22 ± 0.13	7.01 ± 0.15	6.40 ± 0.10	NA
10% MK	6.87 ± 0.14	5.38 ± 0.12	4.75 ± 0.09	4.48[a]
20% MK	6.59 ± 0.08	5.32 ± 0.10	4.66 ± 0.12	NA

NA not available

[a] Only one measurement

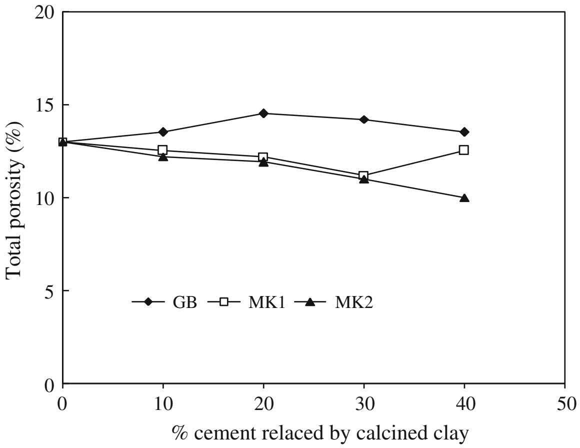


Fig. 4.14 Influence of proportion of cement replaced by each calcined-clay on total porosity [28]

The addition of metakaolin caused reduction in concrete total porosity. The total porosity of metakaolin concrete varied from 7.2 to 11.2%, while control concrete presented a total porosity of 11.1%.

Gonçalves et al. [28] determined the total porosity of mortars prepared with two metakaolin samples and ground calcined-clay brick. Three types of calcined-clays (1) ground calcined-clay brick (GB); (2) commercial metakaolin (MK1) and (3) a calcined-clay produced in the laboratory Metakaolin (MK2). Major constituents of ground calcined-clay brick were SiO_2 (63.89%), Al_2O_3 (25.49%), Fe_2O_3 (7.73%). Major constituents of commercial metakaolin (MK1) were SiO_2 (51.2%), Al_2O_3 (35.3%), Fe_2O_3 (4.0%) whereas laboratory produced metakaolin (MK2) had SiO_2 (52.46%), Al_2O_3 (44.24%), Fe_2O_3 (2.06%). Mortar mixtures 1:1.5, with water/cementitious material ratio of 0.5, were prepared with 10, 20, 30 and 40% of cement was replaced by calcined-clay samples (GB, MK1 or MK2). Total porosity results are shown in Fig. 4.14. It was observed that (1) for all percentages of replacement, the mortar porosity was greater than that of the control sample; and (2) replacement of up to 40% of cement by either one of the metakaolin samples (MK1 or MK2) resulted in a similar continuous reduction in total porosity. This may be attributed, at least in part, to improved packing of the mixtures. Distinct behaviors were found for replacements of 40% cement by the metakaolin samples: whereas replacement by MK1 resulted in a further reduction in porosity, the same was not observed when MK2 was added.

4.5.2 Water Absorption and Sorptivity

Khatib and Mangat [33] demonstrated that sorptivity of concrete; taken from the top surface of a concrete cube can be several times greater than those for concrete taken from the bottom surface. Dias [23] observed that air-cured concrete, over a 4-year period, undergoes an increase in weight and a reduction in sorptivity as a result of carbonation of the surface zone. Also, the greater the initial (6 months) sorptivity, the greater was the reduction in sorptivity (at 4 years) due to carbonation. Equivalent water-cured concrete did not show any drop in sorptivity from carbonation, although sorptivity did decrease with time as a result of continued hydration.

Courard et al. [21] studied the water absorption of mortars containing 0, 10, 15, and 20% metakaolin as partial replacement of cement. One mixture with natural kaolin was also made. The specimens were made with 1:3 with water-cementitious ratio 0.5. Water absorption was measured by total immersion at 28 days and 14 months, and results are given in Table 4.21. It can be observed that (1) water absorption increased with the increase in metakaolin content both at 28 days and 14 months; and (2) at 14 months water absorption was less than that observed at the age of 28 days. Percentage decreased varied from 4.1 to 9.7% for mortar made with MK, and 16.9% with natural kaolin.

Khatib and Clay [36] investigated the effect of metakaolin on the water absorption of concrete. The mixture proportion of control mixture was 1:2.3:3.4 with water–binder ratio of 0.45. Cement was partially replaced with 5, 10, 15 and 20% MK. Tests were conducted up to the age of 90 days from the time of casting. Water absorption (WA) by total immersion is shown in Fig. 4.15. They reported

Table 4.21 Water absorption of mortars made with metakaolin and kaolin [21]

Material	Water absorption (% in mass)		Percentage decrease
	After 28 days	After 14 months	
CEM I 42.5	8.16	7.82	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
10% Kaolin	9.51	7.90	16.9

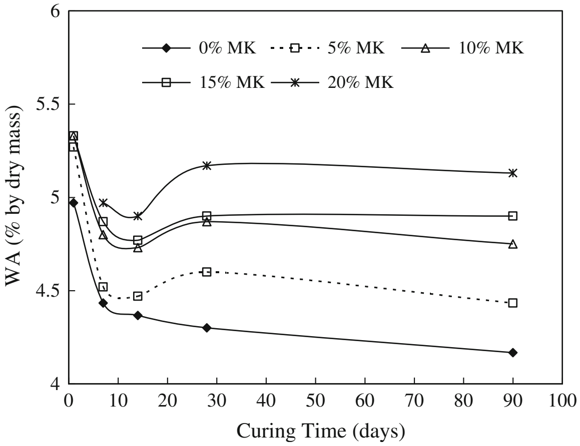


Fig. 4.15 Variation of WA with curing time for concrete containing MK [36]

that (1) water absorption for the control mix decreased with the increase in curing period. The decrease in WA was noticeable during the first 7 days. After 14 days, there was little decrease in WA; (2) a decrease in water absorption capacity was observed for all MK mixes up to about 14 days. Between 14 and 28 days curing period, there was a slight increase in WA caused by the presence of MK. This might be due to the formation of a denser hydration phase. After 28 days, 5 and 10% MK mixes showed a slight decrease in WA, whereas at higher MK replacement levels (15 and 20%), there was little change in WA; and (3) there tends to be a small systematic increase in WA with the increase in MK contents at all curing times. WA values for all mixes ranged between 4.2 and 5.4% by dry mass.

Razak et al. [55] studied the effect of metakaolin on the water absorption and sorptivity of concrete. Cement was replaced with 10% metakaolin. The inclusion of metakaolin greatly reduced the water absorption and sorptivity of concrete when compared with concrete made with OPC.

Badogiannis and Tsivilis [10] determined the sorptivity of concrete mixtures made with Greek kaolin of low kaolinite content (49% metakaolinite, 72.1% SiO_2, 30% active SiO_2) and commercial metakaolin (95% metakaolinite, 54.6% SiO_2, 53% active SiO_2) of high purity. High performance concrete mixtures were made where metakaolin replaced either cement or sand in percentages 10 or 20% by weight of the control cement content. The addition of metakaolin caused a relative decrease in concrete sorptivity. The sorptivity varied from 0.062 to 0.097 mm/min$^{0.5}$, while the PC concrete had sorptivity of 0.114 mm/min$^{0.5}$. Concrete specimens with commercial metakaolin (MKC) demonstrated the best behavior compared to MK concrete specimens and the concrete with MKC as 20% replacement of sand has the lower sorptivity.

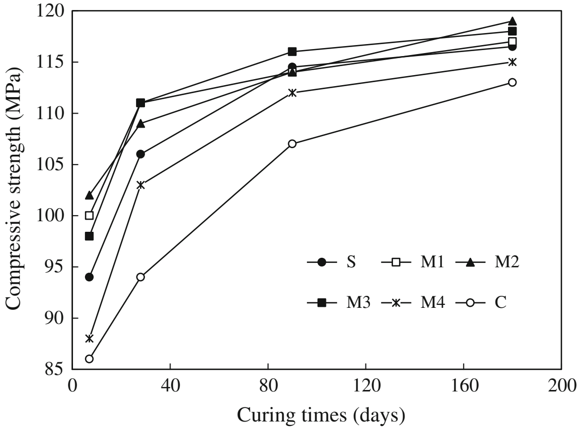
4.5.3 Compressive Strength

Wild et al. [67] determined the compressive strength of concrete made with varying percentages of metakaolin (0, 5, 10, 15, 20, 25, and 30%) up to the age of 90 days. Control concrete mixture proportion was 1:2.3:3.4 with water–binder ratio (w/b) of 0.45. Compressive strength results are presented in Table 4.22.

Table 4.22 Compressive strengths and densities of metakaolin concretes [67]

(MK) (%)	Density (kg/m^3)	Compressive strength (MPa)				
		1-day	7 days	14 days	28 days	90 days
0	2,490	19.07	50.23	57.10	62.60	72.43
5	2,440	21.50	53.80	58.97	63.50	71.63
10	2,460	22.43	62.30	69.23	71.00	80.07
15	2,470	20.23	64.80	74.67	76.00	83.70
20	2,480	19.33	66.47	75.73	82.47	85.13
25	2,470	15.73	62.50	69.77	73.93	82.23
30	2,480	14.53	60.53	72.33	76.73	81.80

Fig. 4.16 Compressive strength versus curing time [22]



They concluded that inclusion of MK enhanced the compressive strength of concrete at all ages, but the optimum replacement level of OPC by MK to give maximum long term strength enhancement was about 20%.

Curcio et al. [22] determined the compressive strength of high-performance mortars containing 15% metakaolin as replacement of cement with a water/binder ratio of 0.33. Four commercially available MK (M1, M2, M3, and M4) samples were used. Major chemical composition (SiO_2 and Al_2O_3) of M1, M2, M3, and M4 metakaolin were; 51.89 and 43.53%; 51.42 and 44.81%; 55.0 and 40.0%; 53.0 and 44.0%, respectively. Silica fume had 96% SiO_2. Figure 4.16 shows the compressive strength development up to the age of 180 days. It was observed that (1) specimens containing three of the four metakaolin samples had a higher rate of compressive strength development as compared to that of the control at ages below 28 days, a consequence of the higher hydration rate; (2) difference in the compressive strength between the specimens with microfillers and control mortar decreased after 28 days, because of a smaller slowdown of the hydration rate in the control; (3) extent of strength enhancement at short curing ages was influenced by the type of cement; it was lower for early strength Portland as compared to ordinary Portland.

Brooks and Johari [14] concluded that inclusion of metakaolin (5, 10, and 15%) as partial replacement of cement increased its 28-day compressive strength (87 MPa) to 91.5, 104, and 103.5 MPa, with 5, 10, and 15% MK content. Poon et al. [49] observed that the cement pastes containing 5–20% 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. Roy et al. [59] also reported increase in compressive strength on addition of MK.

Jin and Li [32] investigated the effect of metakaolin on the mechanical behavior of young concrete under either uniaxial compression or tension. Tests were conducted at ages of 1/2, 1, 2, 3, 7, and 28 days. They reported that (1) stress–strain (deformation) curves for young concretes were different from mature concretes in their capability in resisting the deformation. More ductile behavior was observed for a young concrete. However, the complete stress-deformation curves for young concrete under uniaxial tension showed less ductility as compared to those under uniaxial compression; and (2) metakaolin showed the best enhancement on the mechanical properties of young concrete.

Li and Ding [45] studied the effect of metakaolin (MK) or combination of MK and slag on the 28-day compressive strength of cement mortars. Four series of cement mortars pastes were made. First series (PO) contained 100% cement, 0% MK, and 0% slag; second (M1) 90% cement and 10% MK, 0% slag; third (S2) 70% cement, 10% MK, and 20% slag, and the fourth (S3) 60% cement, 10% MK, and 30% slag. Cement-to-sand ratio was 1:2.5, and w/b ratio was 0.44. Compressive strength results are shown in Fig. 4.17. It was observed that (1) MK enhanced the compressive strength of cement mortar. Concrete containing 10% MK gave the best result; (2) when PC was mixed with MK and ultra-fine slag at the same time, the 3-day compressive strength of S2 and S3 cement mortars was lower than that of PC and cement mortar M1. However, after 7 days, the strengths of S2 and S3 were higher than that of the M1 and PC mortars. After 28 days, the strength of S2 and S3 had greatly surpassed that of the two former cement mortars; and (3) both MK and slag can react with CH release by cement clinker hydration to produce secondary C–S–H gel inside the cement paste. The secondary formed C–S–H gel improved the microstructure of cement paste matrix; therefore, the macroscopic property of cement was also improved. XRD analysis indicated that more $Ca(OH)_2$ was consumed after adding both mineral admixtures.

Poon et al. [50] investigated the performance of metakaolin concrete at elevated temperatures up to 800°C. Normal and high strength concrete (HSC) mixes incorporating 0, 5, 10 and 20% MK were made. They found that (1) after an increase in compressive strength at 200°C; the MK concrete suffered a more severe loss of compressive strength. MK concrete showed a distinct pattern of strength gain and loss at elevated temperatures. A sharp reduction in compressive strength was observed after 400°C followed by severe cracking and explosive spalling.

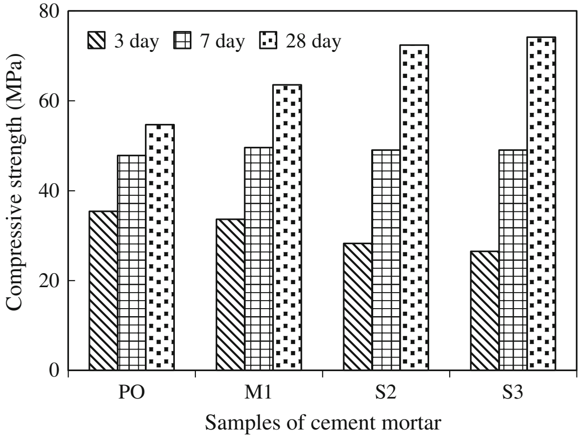


Fig. 4.17 The compressive strength of cement mortars [45]

Within the range 400–800°C, MK concretes suffered more loss and possessed lower residual strengths than the other concretes.

Badogiannis et al. [8] studied the influence of two types of metakaolins; (1) one produced from Poor Greek kaolin (C); and commercial metakaolin (MKC) on the high-performance concrete. Metakaolin was replaced either with cement or sand in percentages of 10 or 20% by weight of the control cement content. The strength of HPC was evaluated using the efficiency factor (*k* value). 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.

Lee et al. [44] reported the compressive strength of mortars incorporating with 0, 5, 10 and 15% of MK by mass. The water-cementitious material ratio (w/cm) was fixed at 0.45 by mass. The cementitious material/fine aggregate was invariant at 2.0 in all mortar mixtures. Table 4.23 presents the data on strength development of mortar specimens cured in tap water. These data indicated that MK15 mortar specimens showed a better compressive strength development compared to MK0 mortar specimens during the entire period of tap water curing.

Badogiannis et al. [9] determined the compressive strength of cement containing five metakaolin up to the age of 180 days. The metakaolinite contents in metakaolins MK1, MK2, MK3, and MK4 (derived from poor Greek kaolins) were 36, 37, 71, and 49%, respectively, whereas it was 95% in a commercial high purity metakaolin (MKC). Cement was replaced with 0, 10, and 20% metakaolins. It was observed that metakaolins had a very positive effect on the cement strength after 2 days and specifically at 28 and 180 days (Table 4.24). This may be because produced metakaolins as well as the commercial-one gave similar hydration

Table 4.23 Strength development of mortar specimens cured in tap water [44]

Mixture	Replacement levels of MK	Compressive strength (MPa)			
		7 days	28 days	91 days	360 days
MK0	0	37.0	48.6	56.8	59.2
MK5	5	33.8	46.3	55.5	60.4
MK10	10	43.2	50.4	56.9	62.2
MK15	15	41.8	51.2	63.0	66.8

Table 4.24 Compressive strength of concrete containing metakaolins [9]

Age (days)	Compressive strength (MPa)											
	PC		MK1		MK2		MK3		MK4		MKC	
	10%	20%	10%	20%	10%	20%	10%	20%	10%	20%	10%	20%
1	17	18	17	16	18	16	21	19	20	18	20	19
2	30	30	28	23	30	24	33	29	32	28	33	29
7	44	44	45	44	48	45	50	50	51	50	54	50
28	57	57	64	68	65	67	66	69	68	65	72	70
180	70	70	79	77	80	75	74	72	80	78	76	76

products after 28 days and the pozzolanic reaction was accelerated between 7 and 28 days, accompanied by a steep decrease of $Ca(OH)_2$ content.

Poon et al. [51] determined the compressive strength of concrete mixes containing 5, 10, and 20% metakaolin as partial replacement of cement. Concrete mixes were prepared with two w/b ratios of 0.3 and 0.5. The maximum nominal size of the coarse aggregate was 10 mm for the concrete with a w/b of 0.3 and 20 mm for the concrete with a w/b of 0.5. The results (Table 4.25) showed that the use of 10% gave the best performance, which resulted in the highest strength increase over the control concretes at all ages, particularly at the age of 3 days. This could be attributed to higher rate of hydration in the metakaolin concrete.

Potgieter-Vermaak and Potgieter [52] studied the compressive strength of mortars containing metakaolin between 10 and 30% up to the age of 28 days. Activation temperature of MK ranged from 550 to 850°C for durations of 30 and 60 min. Mortars were made with sand-cementitious proportion of 3:1 by mass and water: cementitious material ratio of 0.375. It was observed that (1) best activation temperature to produce metakaolin from kaolin is >700°C, and should preferably be at least 750°C; (2) compressive strengths increased with the increase in curing times and depended strongly on the activation temperature. Strength enhancements did not depend significantly on the concentration of metakaolin addition; and (3) longer activation time resulted in marginally higher compressive strengths in the mortars containing MK heated for 60 min compared to those having material heated for 30 min.

Khatib [37] investigated the compressive strength of concrete containing metakaolin (MK) at a low water-to-binder ratio of 0.3. Portland cement (PC) was partially replaced with 0–20% MK. Results of compressive strengths and average density are presented in Table 4.26. Generally, the density tends to increase slightly with increasing amounts of MK in concrete, mainly resulting from the filling effect of MK particles. Compressive strength increased with the increase in time and the incorporation of MK increased the strength beyond 1-day of curing. At 1-day of curing, replacing PC with MK beyond 5% slightly reduced the compressive strength. However, beyond 1-day of curing, MK in the mix increased the compressive strength, and attained a maximum value at 15% MK. Moreover

Table 4.25 Compressive strength of control and blended concretes [51]

Series	w/b ratio	Mix	Total charge passed (C)			
			3 days	7 days	28 days	90 days
1	0.30	Control	68.5	81.1	96.5	102.5
		5% MK	73.0	88.2	103.6	112.9
		10% MK	85.9	99.8	116.8	120.3
		20% MK	70.8	87.6	99.6	113.8
2	0.50	Control	28.6	41.2	52.1	60.4
		5% MK	32.6	45.9	57.1	66.5
		10% MK	40.4	55.2	66.2	71.6
		20% MK	30.0	43.2	58.4	69.1

Table 4.26 Compressive strength of concrete mixes containing MK [37]

MK (%)	Density (kg/m^3)	Age (days)				
		1	7	14	28	56
0	2,293	28.9	55.3	60.7	66.1	71.3
5	2,261	30.6	59.2	67.7	72.5	79.0
7.5	2,316	25.1	62.2	74.4	81.4	85.7
12.5	2,329	28.5	68.6	81.6	85.3	90.4
15	2,337	28.6	70.2	83.6	89.7	91.0
20	2,329	22.8	62.8	78.9	83.2	86.1

the maximum contribution of MK occurred at 14 days of curing where more than 35% increase in strength was obtained.

Gonçalves et al. [28] determined the influence of metakaolin and ground calcined-clay brick on the uniaxial compressive strength of mortar (Fig. 4.18). Three types of calcined-clays (1) ground calcined-clay brick (GB); (2) commercial metakaolin (MK1) and (3) a calcined-clay produced in the laboratory Metakaolin (MK2). Major constituents of ground calcined-clay brick were SiO_2 (63.89%), Al_2O_3 (25.49%), Fe_2O_3 (7.73%). Major constituent of commercial metakaolin (MK1) were SiO_2 (51.2%), Al_2O_3 (35.3%), Fe_2O_3 (4.0%) whereas laboratory produced metakaolin (MK2) had SiO_2 (52.46%), Al_2O_3 (44.24%), Fe_2O_3 (2.06%). Mortar mixtures 1:1.5, with water/cementitious material ratio of 0.5, were prepared with 0, 10, 20, 30, and 40% of cement was replaced by calcined-clay samples (GB, MK1 or MK2). They concluded that (1) compressive strength of mortars made with calcined-clay brick decreased with the increase in calcined-clay percentage in comparison to the control mixture; up to 20%, there was marginal loss in strength, but, at higher levels of replacement (30 and 40%), significant reduction in strength was observed. This may be due to the fact that packing density of the dry mix did not change with the replacement of PC by GB, then it is

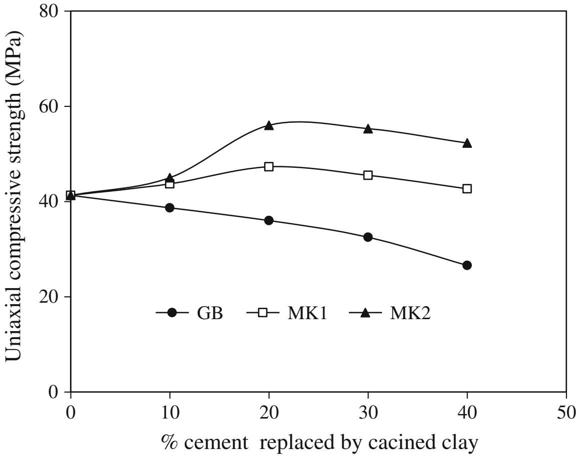


Fig. 4.18 Influence of proportion of cement replaced by each calcined-clay on uniaxial compressive strength of cement mortars [28]

possible to infer that the amount of hydrates formed by the pozzolanic reaction from replacement of up to 20% cement by GB was high enough so that it was able to maintain a constant compressive strength. However, with higher replacement levels, the amount of hydrates resulting from the pozzolanic reaction was probably insufficient to allow maintaining a constant compressive strength, so that the excess of un-reacted GB was only able to contribute in strength due to its physical filler effect; and (2) inclusion of metakaolins (MK1 and MK2) increased the compressive strength of mortar. Optimal results were obtained for 20% replacement of cement by metakaolin, representing increases in 39 and 18% for MK2 and MK1, respectively. This increase may be due to the greater formation of hydrates. At replacement of 30 and 40%, higher compressive strengths than that of the control mixture were observed, but there was reduction in strengths in comparison with 20% replacement. This may probably due to the fact that the more limited availability of calcium hydroxide from the smaller proportion of cement added becomes the limiting factor in the formation of new hydrates. As a result, the unreacted metakaolin can act only as filler.

Janotka et al. [31] determined the compressive strength of cement paste containing Slovak poor metakaolin sands with different metakaolin content [36.0% (MK-1), 31.5 (MK-2) and 40.0% (MK-3)]. The percentage of metakaolin sands was 10, 20 and 40%. It was concluded that (1) control PC paste achieved 43 and 59.6 MPa strength at the ages of 28 and 90 days, respectively. The incorporation of metakaolin sand decreased the strength at 28 days of curing, and decrease in strength was higher as the metakaolin sand content increased. At 28 days, for paste containing MK-1, strength was 41.2, 35.9, and 29.3 MPa whereas strength was 36.8, 28.0, and 14.1 MPa for MK-2 and for MK-3; strength achieved was 32.3, 36.4, and 38.9 MPa; and (2) compressive strength of all paste mixtures increased with age.

4.5.4 Tensile Strength and Elastic Modulus

Qian and Li [53] determined the 28-day direct tensile strength of concrete containing 0, 5, 10, and 15% metakaolin as partial replacement of cement. Specific surface area and average particle diameter of metakaolin were 12,000 m^2/kg and 2.23 μm. Tensile strength results are given in Table 4.27. It was observed that tensile strength increased with the increase in metakaolin content. The average tensile strength increases were 7, 16, and 28% for concrete mixtures made with 5, 10, and 15% MK whereas average ultimate strain increases were 3, 19, and 27%.

Table 4.27 Tensile strength of concrete with different metakaolin replacement [53]

Age (days)	Tensile strength (MPa)			
	MK (0%)	MK (5%)	MK (10%)	MK (15%)
28	3.35	3.58	3.88	4.29

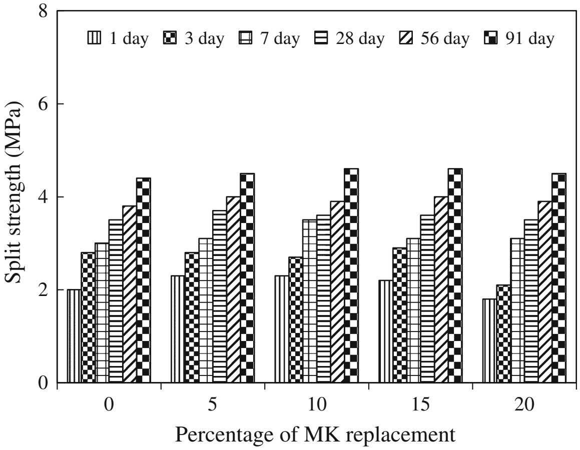


Fig. 4.19 Splitting tensile strength versus replacement of age [38]

The descending area of over-peak stress was less steep when metakaolin replacement was 5 and 10% whereas with 15% metakaolin it was similar to that for concrete without metakaolin. The tensile elasticity modulus for these specimens ranged between 26 and 27 GPa.

Kim et al. [38] presented the results of splitting tensile strength of high-strength concrete made with metakaolin. Cement was replaced with 0, 5, 10, 15 and 20% of metakaolin. Control mixture had 563 kg of cement, 141 kg of fly ash, 532 kg of fine aggregate, 915 kg of coarse aggregate, and 176 kg of water. 28-day compressive strength of control concrete was 60 MPa. Figure 4.19 presents the tensile strength results at the age of 1, 3, 7, 28, 56, and 91 days. This demonstrated the level of tensile strength development according to the replacement ratio of the binder by MK, from 5 to 20%. For binder replacement ratios ranging between 10 and 15%, it was observed that the strength improved with the increase in replacement ratio, while the strength reduced at 20%.

Gonçalves et al. [28] determined the effect of metakaolin samples and ground calcined-clay brick on the modulus elasticity of mortar. Three types of calcined-clays (1) ground calcined-clay brick (GB); (2) commercial metakaolin (MK1) and (3) a calcined-clay produced in the laboratory Mortar mixtures 1:1.5, with water/cementitious material ratio of 0.5, were prepared with 10, and 20% of cement was replaced by calcined-clay samples (GB, MK1 or MK2). Modulus of elasticity of control mortar was approximately 25 GPa. It was observed that increase in replacement of cement by the calcined-clays resulted in a continuous decrease in the elastic modulus of the mortars, reaching reductions up to 10% in comparison to the control mixture. The reduction in the elastic modulus of Portland cement mortars with calcined-clay additions may be probably attributed to the lamellar structure of the clays, which are more deformable under loading. This is associated with the fact that both kaolinite and ilite, even after being calcined at temperatures as high as 550°C and 850°C, respectively, retain their lamellar residual structure.

4.5.5 Bending Strength

Qian and Li [53] investigated the influence of 0, 5, 10, and 15% metakaolin as partial replacement of cement on the bending strength of concrete up to the age of 80 days. Specific surface area metakaolin was 12,000 m^2/kg, with average particle diameter being 2.23 μm. Beam specimens (400 × 100 × 100-mm) were tested under four-point bend on a span of 300 mm. Bending test results are given in Table 4.28. It was observed that (1) 5% metakaolin had little effect on the bending strength of the concrete; (2) at 10 and 15% MK, the 28-day bending strength was increased by 32 and 38%, respectively. At 80 days, increase in bending strength was 13 and 24% for 10 and 15% replacement, respectively. Therefore, significant improvement in bend strength of concrete can be achieved for replacement levels of 10–15% metakaolin.

Courard et al. [21] investigated the role of metakaolin on the bending strength of mortar containing up to 20% metakaolin. The specimens were made with 3 parts of sand, 1 part of cement and 0.5 part of water) in which cement was OPC (CEM I 42.5). Mortar mixtures were made in which cement was replaced by metakaolin (5–20%). One more mixture mix was made with 10% by mass of natural kaolin. Specimens (40 × 400 × 160 mm) were cast and tested up to the age of 28 days. Bending strength results are shown in Fig. 4.20. They concluded that replacement of cement by metakaolin decreased the bending strength during the first days but achieved almost equal strength at the age of 28 days.

Table 4.28 Bending strength of concrete with different metakaolin replacement [53]

Age (days)	Bending strength (MPa)			
	MK (0%)	MK (5%)	MK (10%)	MK (15%)
28	4.65	4.74	6.16	6.40
80	5.70	5.81	6.46	7.06

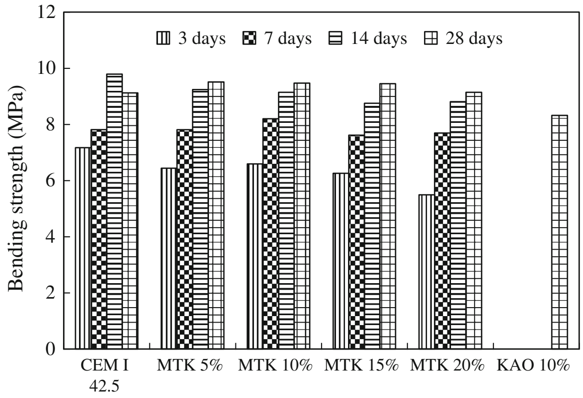


Fig. 4.20 Bending strength of mortars with CEM I 42.5, metakaolin and kaolin [21]

4.5.6 Micro-Hardness

Micro-hardness measurements can contribute to characterization of the properties of the ITZ relative to the bulk cement paste matrix and also helps in estimating the width of the ITZ. Lyubimova and Pinus [46] observed that over a range of water/binder ratios, micro-hardness decreased within 100 μm of the aggregate surface. Whilst reductions in micro-hardness for the ITZ relative to the bulk regions are consistent with the hypothesis that the ITZ is a region of higher than average porosity, such observations are not universal.

Saito and Kawamura [60] reported increase in micro-hardness within 50 μm of the aggregate surface. Igurashi et al. [30] suggested four ITZ/bulk region micro-hardness profiles. For example, in specimens where the microstructure of the ITZ is similar to the bulk region, the close proximity of the aggregate surface can increase micro-hardness values above those recorded for the bulk region by impeding the displacement of material from the indentation site. In contrast, where the ITZ microstructure is weaker than the bulk region, a depression in the micro-hardness profile is expected within the zone of influence of the aggregate, the profile at the aggregate surface also being influenced by the strength of the paste–aggregate bond.

Asbridge et al. [6] determined the variations in the micro-hardness of the hydrated cement matrix as functions of the distance from the aggregate surfaces for specimens in which Portland cement was partially replaced with 0 and 10% of metakaolin. Water/binder ratios were 0.40, 0.50 and 0.60. Cement matrix of mortars were prepared with an aggregate content of 35% by volume. Micro-hardness measurements were made up to distances of 120 μm from the aggregate. Variations in micro-hardness of bulk paste/ITZ are shown in Figs. 4.21, 4.22, 4.23 and 4.24. Figure 4.21 shows that in Portland cement specimens, the ITZ was more porous than the bulk matrix at lower water/binder ratios. The micro-hardness of the ITZ was 22% lower than the bulk matrix at a water/binder ratio of 0.40,

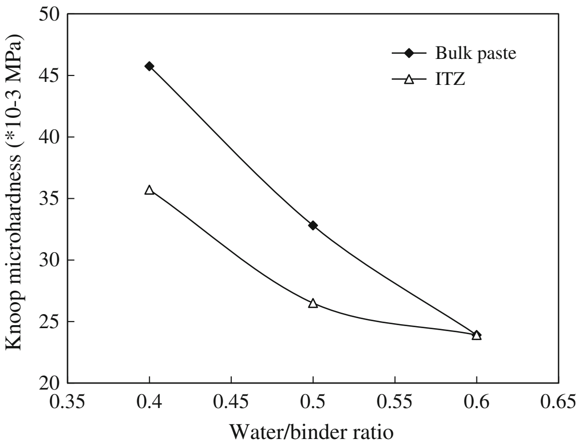


Fig. 4.21 Variation in micro-hardness of bulk paste and ITZ with water/binder ratio (Portland cement binder) [6]

Fig. 4.22 Variation in micro-hardness of bulk paste and ITZ with water/binder ratio (Portland cement/metakaolin binder) [6]

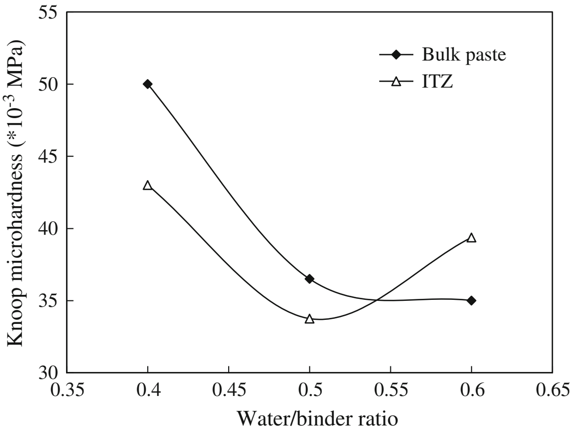


Fig. 4.23 Variation in micro-hardness of bulk paste with water/binder ratio and binder composition [6]

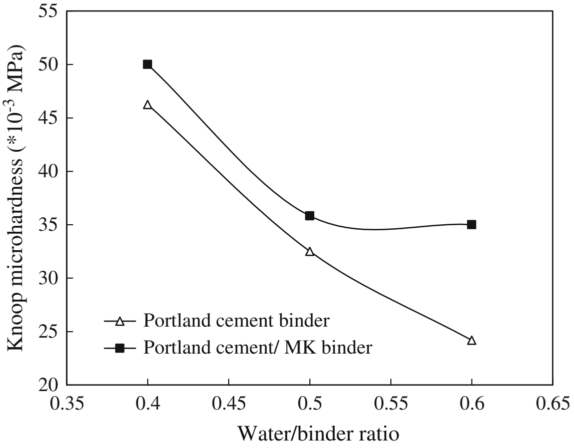
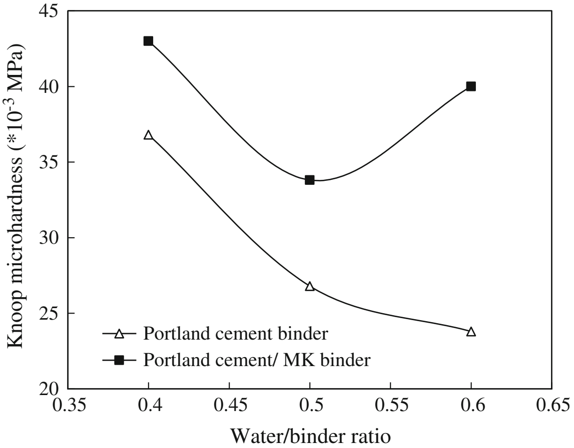


Fig. 4.24 Variation in micro-hardness of ITZ with water/binder ratio and binder composition [6]



and was 18% lower at a water/binder ratio of 0.50. Figure 4.22 indicates that in the specimens prepared with 10% metakaolin, the micro-hardness of the ITZ was similar to that of the bulk matrix. From Figs. 4.23 and 4.24, it is clear that micro-hardness of the bulk matrix and, to a greater degree, the ITZ increased when metakaolin was used.

4.6 Durability Properties of Concrete Containing Metakaolin

4.6.1 Alkali–Silica Reaction

Ramlochan et al. [54] examined the influence of high-reactivity metakaolin (HRM) in controlling expansion due to alkali–silica reaction (ASR) of concrete containing 0–20% HRM as a partial replacement for OPC, up to 2 years. Two types of alkali–silica reactive aggregates: a siliceous limestone (Spratt) and greywacke–argillite gravel (Sudbury) were used. The major chemical compounds in cement were; SiO_2 (19.97%), CaO (62.69%), Al_2O_3 (5.08%), Fe_2O_3 (2.26%), MgO (2.66%), Na_2O (0.30%). Concrete prisms (75 × 75 × 300 mm) were cast with each coarse reactive aggregate, a non-deleteriously reactive sand and high-alkali Portland cement with a 1.02% equivalent soda content (or Na_2O). Prisms containing the Spratt aggregate were cast with 0, 5, 10, 15, and 20% HRM as a partial cement replacement, and prisms containing the Sudbury aggregate were cast with 0, 10, and 15% HRM replacement levels. The accelerated mortar bar method was used. Figures 4.25 and 4.26 show the expansion evolution of concrete prisms stored at 38°C and 100% RH containing different levels of HRM for the two reactive aggregates. It was observed that expansion decreased with the increase in HRM content. Both control specimens (0% HRM) exceeded the expansion limit criterion of 0.04%. The siliceous limestone aggregate (Spratt) reacts very rapidly and control specimens exceeded 0.04% expansion at 56 days.

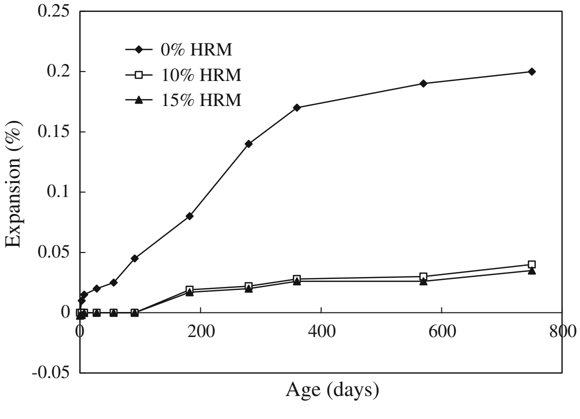


Fig. 4.25 Expansion evolution of CAN/CSA A23.2-14A concrete prisms containing HRM and Sudbury aggregate [54]

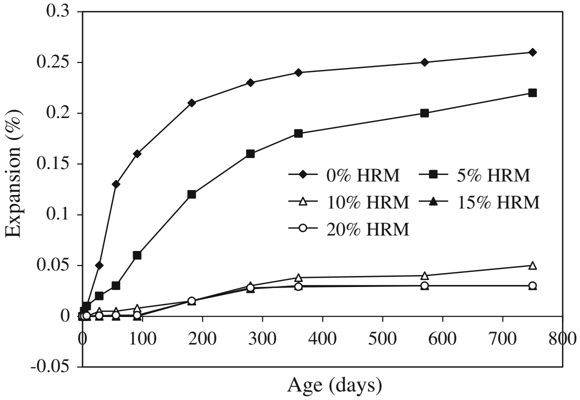


Fig. 4.26 Expansion evolution of CAN/CSA A23.2-14A concrete prisms containing HRM and Spratt aggregate [54]

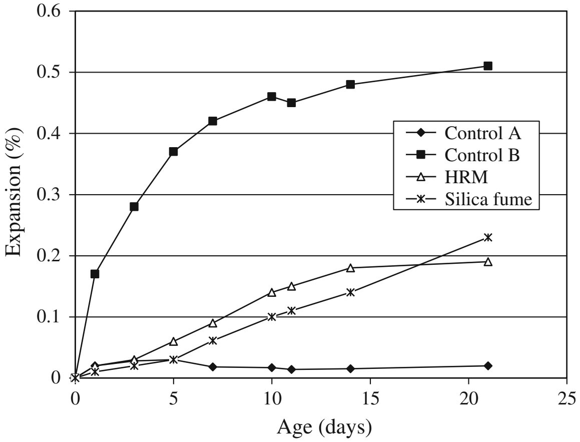
The greywacke aggregate (Sudbury) is slower reacting, but exceeded 0.04% expansion at about 150 days. Both control specimens also exhibited visual signs of distress early on; surface cracking with exuded gel and an associated white streaking was observed in Spratt control prisms at 90 days and in Sudbury control prisms at 180 days.

Aquino et al. [3] studied the influence of high-reactivity metakaolin (HRM) and silica fume on the alkali–silica reaction of mortar. A high-alkali cement (0.46% Na_2O, 1.06% K_2O, 1.17% Na_2O eq). The oxide composition of HRM ($Al_2O_3 + SiO_2 + Fe_2O_3$) was 95.3%, and silica fume had SiO_2 content of 93%. Four different mortar mixes were prepared with water-to-cementitious materials ratio of 0.56 and aggregate-cementitious ratio of 2.25. Control mixture A contained no mineral admixture. In two other mixtures, cement was replaced with 10% of SF and HRM. Control mixture B contained high-alkali cement and reactive aggregates, but no mineral admixture. Mortar bars of size 25 × 25 × 280 mm were made. The expansion measurements were made at the age of 1, 3, 5, 7, 14, and 21 days of curing in 1 N NaOH solution. Results of expansion measurements are shown in Fig. 4.27. It was observed that (1) control A mixture, which did not incorporate any reactive aggregate, did not show any significant expansion; (2) Control B mixture which contained reactive aggregate but did not incorporate either SF or HRM, expanded at a faster rate and reached expansions of 0.48 and 0.51% at 14 and 28 days; and (3) mortar bars containing HRM or SF showed significantly lower expansion at all ages.

4.6.2 Chloride-Ion Diffusion/Permeability

Zhang and Malhotra [71] measured the chloride penetration resistance (ASTM C1202) of PC concrete and PC-10% MK concrete. The concrete with w/b ratio 0.40 was moist-cured for 28 and 91 days prior to being subjected to electrical conductivity measurements. The PC–MK concrete showed significantly lower

Fig. 4.27 Influence of HRM and SF on mortar bar expansion over a period of 21 days after immersion in 1 N NaOH at 80°C [3]



conductivity values than the PC concrete. Cabrera and Nwaubani [16] measured the effective chloride diffusion coefficients of PC and PC-15% MK (for two different MKs) pastes using a chloride diffusion cell. The pastes of w/b ratio 0.40 were moist-cured (100% RH) for 60 days. PC–MK pastes gave lower chloride diffusion coefficients than the PC paste.

Thomas et al. [66] studied the chloride binding capacity of cement paste with and without 8% HRM by exposing dried paste samples to various concentrations of NaCl solution and determining the amount of chloride removed from solution on establishment of equilibrium. For up to a 1-M solution concentration, the binding capacities of the two pastes were similar but above this concentration, the binding capacity of the HRM paste increased at a much greater rate with increased solution concentration than did the pure PC paste.

Boddy et al. [13] and Gruber et al. [29] measured the chloride diffusion at the age of 365 and 1,095 days. The apparent diffusion coefficients were reduced with age and on decreasing the w/b ratio. It also showed marked decreases with increasing HRM content.

Asbridge et al. [5] studied the effect of metakaolin and aggregate content on the diffusion kinetics of chloride ions in hydrated Portland cement mortars (Table 4.29) under steady- and non-steady-state conditions. In cement mortars, cement was replaced with 10% metakaolin. It was concluded that (1) the steady-state diffusivity of chloride ions in mortar pastes incorporating metakaolin did not vary significantly with aggregate volume fractions. Mortar-paste capillary porosity data showed only some increases at aggregate volume fractions greater than 40%;

Table 4.29 Composition of pastes and mortars [5]

	Steady state	Non-steady state
Binder	PC/MK	PC, PC/MK
Water/binder ratio	0.35	0.40
Aggregate contents (% vol)	0, 15, 30, 40, 50, 55	0, 15, 35, 55

Table 4.30 Chloride diffusion rates for mortars with CEM I 42.5, metakaolin and kaolin [21]

Material	Breakthrough time (days)	Apparent diffusion coefficient (m^2/s)
CEM I 42.5	13	1.29×10^{-12}
5% Metakaolin	45	4.71×10^{-12}
10% Metakaolin	82	3.31×10^{-12}
15% Metakaolin	203	1.23×10^{-12}
20% Metakaolin	Not after one year	–
10% Kaolin	4	1.81×10^{-12}

(2) non-steady-state chloride diffusivities of mortar pastes increased with aggregate volume in samples with only Portland cement as binder; (3) the capillary porosity of the mortar paste increased with aggregate volume, indicating that the ITZ had a higher overall porosity than the bulk paste; and (4) the use of 10% metakaolin as a partial replacement for Portland cement reduced non-steady-state chloride diffusivities by approximately one-order of magnitude relative to those samples with only Portland cement as binder. Mortar-paste diffusivities did not vary significantly with variations in aggregate content. Relative to control samples, metakaolin reduced mortar-paste capillary porosities although the latter still increased with increasing aggregate volumes. The lack of variation in mortar-paste diffusivity and rising capillary porosity with increasing aggregate content supports the hypothesis that the use of metakaolin increases permeation path tortuosity and inhibits percolation.

Courard et al. [21] investigated the effect of metakaolin on the chloride diffusion rates of mortars. Metakaolin percentages as partial replacement of cement were 0, 10, 15, and 20%. One mixture with natural kaolin was also made. Mixture proportion of mortar was 3 parts of sand, 1 part of cement, with w/c ratio of 0.5. Diffusion rates of Cl^- and Na^+ ions into cement mortars were monitored using two-compartment diffusion cells. At periodic intervals, chloride concentration was measured by titration from a 20 cm^3 sample of the solution. The evolution of chloride diffusion was measured for 314 days for cement, metakaolin and kaolin (Table 4.30). The breakthrough time was calculated from the intercept of the concentration versus time date. Breakthrough time represents the time necessary for the initiation of Cl^- ion transfer through the sample. It gives a view of the porous skeleton. Mortar with 20% MK gave the best results as even after 1 year, no diffusion was observed. An increase from 10 to 15% metakaolin content seemed to induce an increase of 150% of occurrence time and a decrease of 170% for diffusion coefficient. Kaolin had no effect and seemed on the contrary to accelerate the phenomenon of diffusion in comparison with the reference mix.

Poon et al. [51] studied the effect of metakaolin on the chloride penetrability of the concrete mixes (Table 4.31). Concrete mixes were prepared with two w/b ratios of 0.30 and 0.50. Cement was replaced with 5, 10, and 20% metakaolin. The maximum nominal size of the coarse aggregate was 10 mm for the concrete with a w/b of 0.30 and 20 mm for the concrete with a w/b of 0.50. It was observed that MK concretes showed lower total charges passed than the control. At the w/b of

Table 4.31 Chloride permeability of control and blended concretes [51]

Series	w/b ratio	Mix	Total charge passed (C)			
			3 days	7 days	28 days	90 days
1	0.30	Control	2,461	2,151	1,035	931
		5% MK	1,327	1,244	862	646
		10% MK	417	347	199	135
		20% MK	406	395	240	124
2	0.50	Control	5,312	4,054	2,971	2,789
		5% MK	4,215	3,765	2,079	1,065
		10% MK	1,580	1,247	918	752
		20% MK	751	740	640	580

0.3, concrete with a 10% MK replacement showed the best performance, while at the w/b of 0.50, concrete with a 20% replacement was the best.

Badogiannis and Tsivilis [10] determined the chloride and gas permeability of concretes made with Greek kaolin of low kaolinite content (49% metakaolinite, 72.1% SiO_2, 30% active SiO_2) and commercial metakaolin (95% metakaolinite, 54.6% SiO_2, 53% active SiO_2) of high purity. Concrete mixtures were made in which metakaolin replaced either cement or sand in percentages 10 or 20% by weight of cement. Chloride and gas permeability results are given in Table 4.32. The addition of metakaolin caused a significant increase of concrete resistance to chloride penetration. The charge passed (in the rapid chloride test) in metakaolin concrete varied from 180 to 820 C, while charge passed in PC concrete was 2,460 C. Concrete with MKC and 10% replacement of sand exhibited higher resistance to chloride penetration. Concrete with metakaolin exhibited lower gas permeability values compared with PC concrete. The gas permeability of the metakaolin concrete varied from 1.35 to 1.85×10^{-16} m^2, while the control concrete presented a gas permeability of 2.94×10^{-16} m^2. The concrete with MK and 10% replacement of cement showed lower gas permeability.

Kim et al. [38] studied chloride permeability of high-strength concrete made with Korean metakaolin. Cement was replaced with 0, 5, 10, 15 and 20% of metakaolin. Control mixture had 563 kg of cement, 141 kg of fly ash, 532 kg of fine aggregate, 915 kg of coarse aggregate, and 176 kg of water. 28-day

Table 4.32 Chloride and gas permeability of concrete mixtures [10]

Mixture	Chloride permeability (C)	Gas permeability ($m^2 \times 10^{-16}$)
Control concrete	2,460	2.94
MKC-CR10	730	1.68
MKC-CR20	240	1.45
MK-CR10	690	1.35
MK-CR20	760	1.60
MKC-SR10	180	1.75
MKC-SR20	530	1.56
MK-RR10	820	1.71
MK-SR20	390	1.85

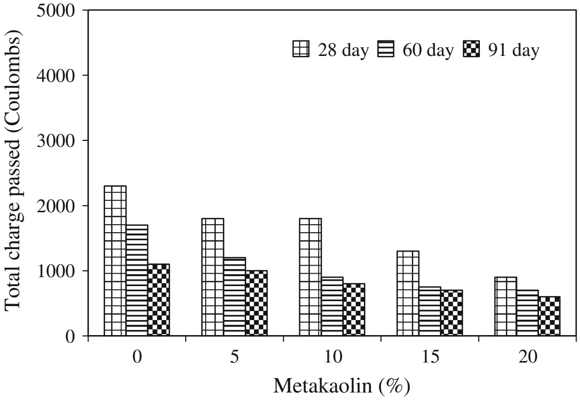


Fig. 4.28 Total charge passed versus replacement level with metakaolin [38]

compressive strength of control concrete was 60 MPa. The resistance of concrete to chloride attack was assessed by rapid chloride permeability test (RCPT) at 28, 56 and 91, and the results are shown in Fig. 4.28. The permeability appeared to decrease as the replacement ratio and curing time increased. Also, all of mixtures with MK revealed very low level of permeability. The increase in resistance to chloride permeability is due to the continued hydration and pozzolanic reaction, accompanied by a decrease in porosity and pore sizes.

Gonçalves et al. [28] investigated the chloride ion penetration of mortars mixtures prepared with metakaolin samples and ground calcined-clay brick. Three types of calcined-clays (1) ground calcined-clay brick (GB); (2) commercial metakaolin (MK1) and (3) a calcined-clay produced in the laboratory Metakaolin (MK2). Major constituents of ground calcined-clay brick were SiO_2 (63.89%), Al_2O_3 (25.49%), Fe_2O_3 (7.73%). Major constituents of commercial metakaolin (MK1) were SiO_2 (51.2%), Al_2O_3 (35.3%), Fe_2O_3 (4.0%) whereas laboratory produced metakaolin (MK2) had SiO_2 (52.46%), Al_2O_3 (44.24%), Fe_2O_3 (2.06%). Mortar mixtures 1:1.5, with water/cementitious material ratio of 0.5, were prepared with 10, and 20% of cement was replaced by calcined-clay samples (GB, MK1 or MK2). They concluded that chloride-ion penetration in control mixture was 13,487 C. The use of calcined-clay promoted a general reduction in the chloride charge. Chloride-ion penetration in mortar mixtures with ground calcined clay brick was 8,460 and 2,111 coulombs; reduction from 1.5 to 6 times for mixtures containing 10 and 20% GB, respectively, whereas this reduction was even more significant, by 10 and 31 times for mixtures containing 10 and 20% MK1, respectively, in comparison to the control mixture. This may be because of the resistance to chloride-ion penetration is more directly associated to the refinement of the pore structure.

4.6.3 Hydroxide Ion Diffusion

Coleman and Page [20] studied the hydroxide ion concentrations of pore solutions of ordinary Portland cement pastes containing 0, 10 and 20% of metakaolin by

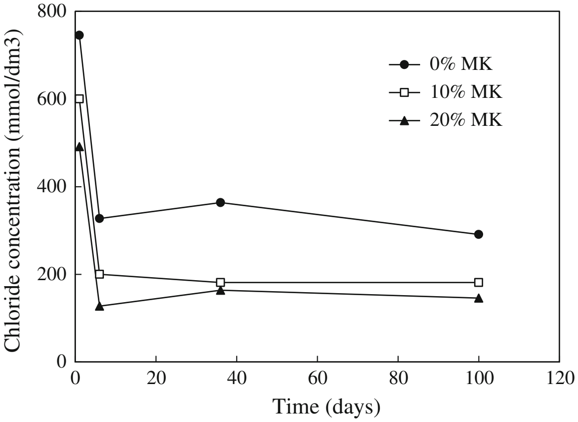


Fig. 4.29 Effect of additions of MK501 on pore solution chloride ion concentration for samples containing 1.0% internal chloride ions (by weight of total solids) [20]

weight of cement at various stages of hydration. Blended cements were prepared from OPC and two grades of metakaolin, labeled as MK501 (major elements; SiO_2 54.2%; Al_2O_3 40.8%) and MK505 (major elements; SiO_2 52.1%; Al_2O_3 41%), of differing composition with respect to minor contaminants. Blended cement pastes were made by partial replacement of OPC with metakaolin having water/solids ratio of 0.5. The effects of metakaolin on the pore solution chloride ion concentrations for samples containing 1.0% of internal chloride ions are shown in Figs. 4.29 and 4.30.

It was observed that both grades of metakaolin caused a substantial reduction in the concentrations of free chloride ions that were retained in the pore solution phase of paste specimens in which 1% chloride (by weight of total solids) had been included as a mix contaminant. This effect was also observed for specimens made from the 501 grade of metakaolin with 0.4% chloride. In specimens with only 0.1% chloride as a mix contaminant, the capacity of the cement hydration products to bind chloride ions was such that the concentrations of chloride remaining in the

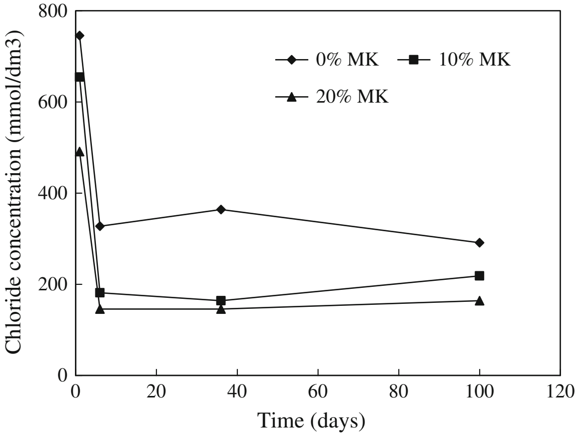


Fig. 4.30 Effect of additions of MK505 on pore solution chloride ion concentration for samples containing 1% internal chloride ions (by weight of total solids) [20]

pore solution at ages of 36 days or longer had fallen to around 10 mmol dm^{-3}, irrespective of whether the material contained 0, 10 or 20% metakaolin.

4.6.4 Sulfate Resistance

Sulfate attack is one of the most aggressive environmental deteriorations that affect the durability of concrete structures. The sulfate attack on concrete leads to expansion, cracking, and deterioration of many civil engineering structures exposed to sulfate environment such as piers, bridges, foundations, concrete pipes, etc. The sulfate attack is generally attributed to the reaction of sulfate ions with calcium hydroxide and calcium aluminate hydrate to form gypsum and ettringite. The gypsum and ettringite formed as a result of sulfate attack is significantly more voluminous (1.2 to 2.2 times) than the initial reactants. The formation of gypsum and ettringite leads to expansion, cracking, deterioration, and disruption of concrete structures. In addition to the formation of ettringite and gypsum and its subsequent expansion, the deterioration due to sulfate attack is partially caused by the degradation of calcium silicate hydrate (C–S–H) gel through leaching of the calcium compounds. This process leads to loss of C–S–H gel stiffness and overall deterioration of the cement paste matrix.

Khatib and Wild [35] investigated the effect of metakaolin on the sulfate resistance of mortar. Two types of cements were used; high C_3A and intermediate C_3A content. Cement was replaced with 0, 5, 10, 15, 20, and 25% of metakaolin (MK). Specimens of size 25 × 25 × 285 mm were moist-cured in air for 14 days, and their length was measured before immersing in 5% Na_2SO_4 solution. Test results demonstrated that (1) expansion decreased systematically with the increase in MK content for both types of cement; (2) for mortars containing high C_3A cement, the control mortar and mortars containing 5 and 10% MK showed rapid expansion and deterioration between 40 and 70 days exposure to sulfate solution. Mortars containing 15 and 20% MK showed small but quite sharp expansions also between 40 and 70 days, but subsequently stabilized. By 520 days, mortar containing 20 and 25% MK showed no significant changes in length; (3) with intermediate C_3A content in cement, trend was similar to the mortars made with high C_3A content. The control mortar (0% MK) showed significant expansion followed by 5% MK mortar. Mortar containing 10% MK exhibited little expansion and other mortar specimens containing 15, 20 and 25% were found to be extremely stable, showing little overall change and no sign of deterioration after 520 days of exposure in sodium sulfate solution.

Courard et al. [21] studied the sulfate resistance of mortars containing 0, 10, 15, and 20% metakaolin as partial replacement of cement. One mixture with natural kaolin was also made. The specimens were made with 1:3 with water-cementitious ratio 0.5. Resistance to sulfate was determined by measuring the changes in length of prismatic specimens when stored in a standard sulfate solution. At the age of 28 days, the specimens were measured for length and placed in the sulfate solution having a concentration of 16.0 ± 0.5 g/l SO_4^{2-} and prepared by adding sodium sulfate (Na_2SO_4) to water. Corresponding control specimens were placed in limewater. Changes in length were measured after storage periods of 4, 8, 12, 16, 20, 28, 40 and 52 weeks at 23 ± 2°C. It was observed that OPC mortar exhibited expansion only after few days. Variation in length after only 84 days was 3.7%. Behaviors of metakaolin-modified mortar in comparison with reference mortar, an inhibition of sulfate attack was observed, especially for more than 10% replacement of cement part metakaolin, by consuming $Ca(OH)_2$, has a large positive effect on mortar durability in the sulfate environment.

Lee et al. [44] examined the resistance of mortars made with varying percentages of metakaolin (MK), exposed to magnesium sulfate solutions. The resistance of mortar specimens was evaluated by expansion and compressive measurements. Cement was partially replaced with 0, 5, 10 and 15% of MK by mass. The cementitious material/fine aggregate ratio was maintained at 2 with water-cementitious material ratio as 0.45. All mortar and paste samples were immersed in magnesium sulfate solution ($MgSO_4$) for 360 days. Sulfate solution concentrations were 0.42% (3,380 ppm of $SO4^{2-}$), 1.27% (10,140 ppm of $SO4^{2-}$) and 4.24% (33,800 ppm of $SO4^{2-}$), respectively. Results of expansion of mortars at 360 days and reduction in compressive strength are shown in Figs. 4.31 and 4.32, respectively. It was observed that with the increase in concentration from 0.42 to 4.24% resulted in a large increasing expansion, with increasing the solution concentrations. However, 0.42% had little effect on expansion. This implied the possible presence of the critical concentration influencing the expansion of mortar specimens with or without MK. However, with respect to the reduction in the compressive strength of mortar specimens attacked by magnesium sulfate solution, a general trend indicating an almost linear increase of values in the reduction in compressive strength at 360 days with the increase in concentration of the solutions was observed.

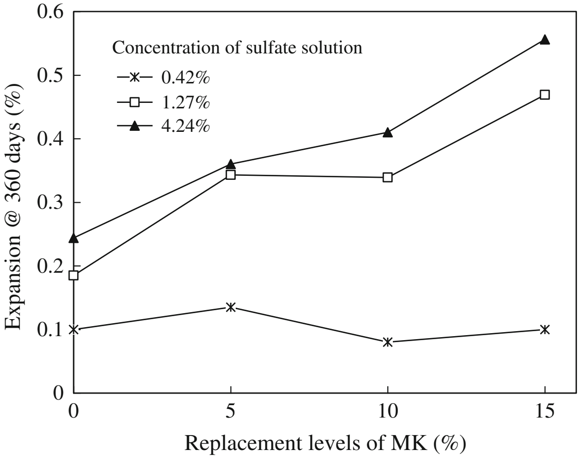


Fig. 4.31 Effect of solution concentrations and MK replacement levels on the expansion of mortar specimens exposed to magnesium sulfate solution [44]

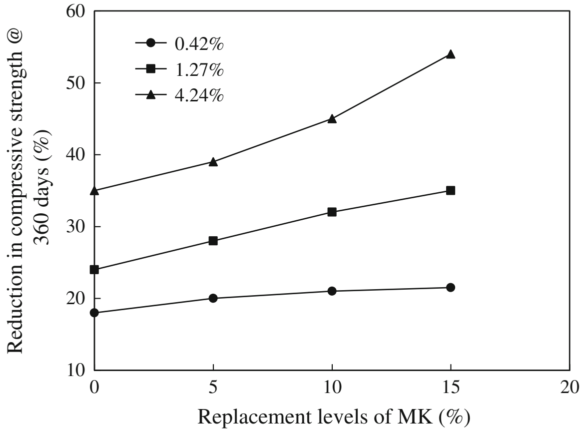


Fig. 4.32 Effect of solution concentrations and MK replacement levels on the reduction in the compressive strength of mortar specimens exposed to magnesium sulfate solutions [44]

Al-Akhras [1] investigated the durability of concrete made with metakaolin (MK) subjected sulfate attack. MK contents were 5, 10, and 15% as partial replacement of cement. Concretes were made with two w/b ratios of 0.50 and 0.60. The other experimental parameters were: initial moist curing period (3, 7, and 28 days), curing type (moist and autoclaving), and air content (1.5 and 5%). The degree of sulfate attack was determined by measuring the expansion of concrete prisms (75 × 75 × 300 mm).

The effect of MK replacement level on the variation of sulfate expansion is shown in Figs. 4.33 and 4.34. It was concluded that (1) the sulfate resistance of MK concrete was higher than that of plain concrete. Sulfate resistance of MK concrete increased with the increase in MK content. Plain concrete was not durable to sulfate attack, reaching maximum sulfate expansion values of 0.4 and 0.45% after 18 months at w/b ratios of 0.50 and 0.60, respectively; (2) the 10 and 15% MK concrete at both w/b ratios showed excellent durability to sulfate attack. The sulfate expansion was 0.10 and 0.07% for concrete at w/b ratio of 0.50, and 0.13

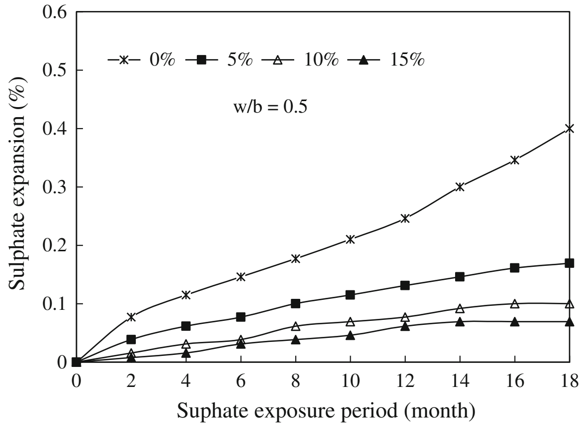
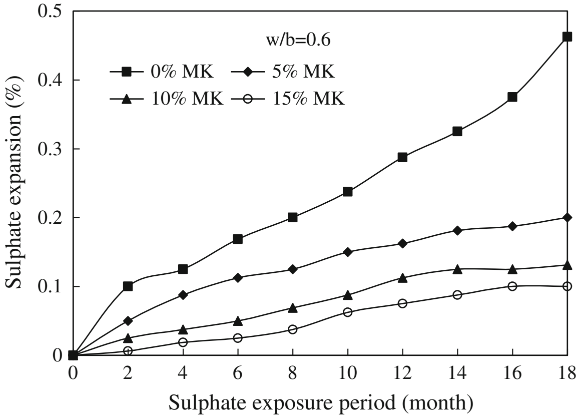


Fig. 4.33 Effect of metakaolin replacement level on the variation of sulfate expansion with sulfate exposure period at w/b ratio of 0.50 [1]

Fig. 4.34 Effect of metakaolin replacement level on the variation of sulfate expansion with sulfate exposure period at w/b ratio of 0.60 [1]



and 0.10% for concrete at w/b ratio of 0.60, respectively; (3) MK (5%) concrete showed intermediate durability to sulfate attack reaching maximum sulfate expansion values of 0.17 and 0.2% for concrete at w/b ratios of 0.50 and 0.60, respectively. The enhancement in the sulfate resistance of concrete with the increase in MK content can be explained by the following mechanisms. First, the replacement of a portion of Portland cement with MK reduces the total amount of tricalcium aluminate hydrate in the cement paste matrix of concrete. The second mechanism is through the pozzolanic reaction between MK and calcium hydroxide released during the hydration of cement, which consumes part of the calcium hydroxides. Thus, the quantity of expansive gypsum formed by the reaction of calcium hydroxide will be less in MK concrete than in plain concrete. Furthermore, the formation of secondary C–S–H by the pozzolanic reaction, although less dense than the primary C–S–H gel, is effective in filling and segmenting large capillary pores into small, discontinuous capillary pores through pore size refinement, decreasing the total permeability of concrete. In addition to the pozzolanic reaction, the filler action of MK due to the fine particle size of MK (1 μm) compared to the particle size of cement (12 μm) further densifies the pore structure of MK concrete to enhance the resistance of MK concrete to sulfate attack.

Kim et al. [38] examined the resistance of mortars containing metakaolin. The resistance to acid attack was assessed by immersion test in 2% sulfuric acid solution until 8 weeks after 28 days of water curing. Seven mix proportions of mortar were made with 0, 5 and 15% MK content having w/b ratio of 0.50. Significant reduction in compressive strength of concrete mixtures containing metakaolin was observed compared control mixture. The compressive strength at 56 days revealed a reduction ratio of about 20% compared to the specimens replaced with 5 and 15% of MK. Test results related to the resistance of mortar to sulfuric acid verified that the reduction rate of the compressive strength at 56 days was similar for replacement rates of 5 and 15% by metakaolin.

4.6.5 Corrosion Résistance

Batis et al. [11] investigated the influence of metakaolin on the corrosion resistance of cement mortar. A poor Greek kaolin with low kaolinite content was thermally treated and the produced metakaolin (MK) was ground to the appropriate fineness (20% residue at 13.6 μm). In addition, a commercial metakaolin (MKC) of high purity was also used. For the corrosion measurements, mortar mixes were made by replacing cement or sand with 10 and 20% of metakaolin. For the corrosion measurements, mortar specimens were then exposed to the corrosive environment of either partial or total immersion in 3.5% w/w NaCl solution. The corrosion tendency of the reinforcing steel bars was estimated in all types of the mortar specimens, by half-cell potential development versus the exposure time in the corrosive environment. Plots of this evolution are shown in Fig. 4.35. Initially the potential values of almost all specimens immersed in chloride environment equal −200 mV versus saturated calomel electrode (SCE). Thereafter decay was observed to more negative values and finally after 8 months of exposure it differentiates between the various specimens. It is well established (C876, 1991) regarding the significance of the numerical value of the potentials that, if potentials over an area are numerically less than 0.200 V versus SCE, there is a greater than 90% probability that there is no corrosion of the reinforcing steel bars at the time of measurement, whereas if potentials over the examined area fluctuate between −0.200 and −0.350 V versus SCE, the corrosion activity of the reinforcing steel is uncertain. Finally, if potentials are numerically greater than −0.350 V versus SCE, there is a greater than 90% probability that corrosion of reinforcing steel bars occurs.

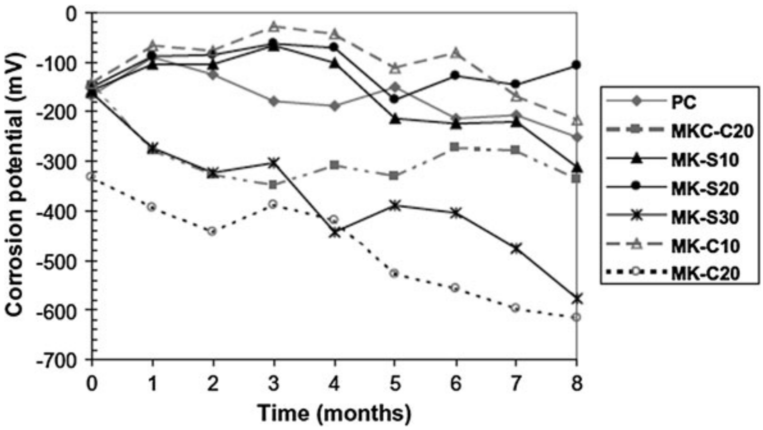
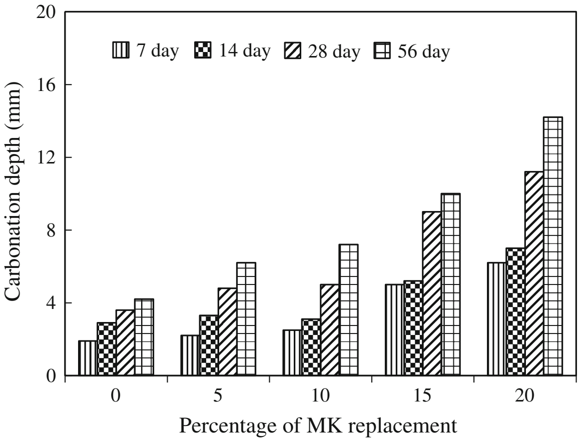


Fig. 4.35 Corrosion resistance of cement mortar [11]

Fig. 4.36 Carbonation depth versus replacement level of metakaolin [38]



4.6.6 Carbonation

Kim et al. [38] studied the effect of metakaolin on the carbonation of high-strength concrete. Cement was replaced with 0, 5, 10, 15 and 20% of metakaolin. Control mixture had 563 kg of cement, 141 kg of fly ash, 532 kg of fine aggregate, 915 kg of coarse aggregate, and 176 kg of water. The resistance of concrete to carbonation was assessed by the phenolphthalein indicator method. The accelerated conditions were 5% CO_2, 60% RH and 30°C. The carbonation depth of concrete was measured at 7, 14, 28 and 56 days, and the results are shown in Fig. 4.36. It was observed that the carbonation depth of concrete mixtures increased with increase in metakaolin content, and also with age. At 28 days, carbonation depth of concrete increased by 20–30% with MK content of 5 and 10%, whereas carbonation depth increased by 40 and 70% at 56 days. On the other hand, the carbonation depth increases to about 100–370% for replacement ratios of 15 and 20% regardless of the age of concrete. It is probably due to the fact that the replacement of cement by MK decreases the content of portlandite in hydrate products due to pozzolanic reaction.

4.6.7 Creep and Shrinkage

Wild et al. [69] showed that, for cement–MK pastes (w/b = 0.55), autogenous shrinkage increased for MK content up to a maximum of 10%; then, it appeared to be comparable to that of the control cement paste for MK content above 15%. An expansion up to 14 days for all the compositions (0–25% MK) was also observed, except for 10% MK. Kinuthia et al. [39] also found, in cement–MK pastes (w/b = 0.50), that 5 and 10% MK increased the autogenous shrinkage of cement pastes, while at 15 and 20% MK, they observed a significant decrease. The effect of MK on autogenous shrinkage of cement pastes can be the consequence of four phenomena: (1) cement dilution by MK, less cement generating less shrinkage, (2) heterogeneous nucleation of hydrates on the surface of MK particles, accelerating cement hydration and, consequently, increasing shrinkage, (3) pozzolanic reaction of MK with CH produced by cement and, (4) increase of capillary tension, due to the refinement of pore size distribution, leading to an increase in autogenous shrinkage.

Brooks and Johari [14] studied the effect of metakaolin (MK) on creep and shrinkage of concrete mixtures containing 0, 5, 10, and 15% of MK. Control concrete mixture proportion was 1:1.5:2.5 with a water-to-cement ratio of 0.28. Autogenous shrinkage was measured from the time of initial set to 24 h and from 24 h till 200 days. Total shrinkage consists of autogenous shrinkage from 24 h and drying shrinkage due to water loss to environment. The results of autogenous, total shrinkage and creep are given in Tables 4.33 and 4.34. It was concluded that (1) at very young ages, autogenous shrinkage was reduced with the increase in MK content. After 24 h, autogenous shrinkage of MK15 concrete was reduced by 65% in comparison with OPC concrete. The reduction of autogenous shrinkage could be due to the dilution effect which is caused by reduction in cement content; (2) at long-term, autogenous shrinkage increased with the increase in MK content. At 200 days, there were 91, 80, and 56% increase in autogenous shrinkage of concrete with 5, 10, and 15% MK content, respectively; and (3) inclusion of MK reduced both total and basic creep of concrete, with a greater reduction in creep at higher replacement levels. The reduction in creep could be attributed to a denser pore structure, stronger paste matrix and improved paste aggregate interface of MK concretes as a result of the formation of additional hydrate phases from secondary

Table 4.33 Results for the 200-day total and autogenous shrinkage of concrete [14]

Item/concrete mixtures	OPC	MK5	MK10	MK15
Total shrinkage from initial set (10^{-6})	861	713	618	516
Total shrinkage from 24 h (10^{-6})	558	499	455	410
Total autogenous shrinkage from initial set (10^{-6})	445	485	419	327
Autogenous shrinkage 24 h (10^{-6})	142	271	256	221
Percentage of A.S.–T.S. from initial set	52	68	68	63
Percentage of A.S.–T.S. from 24 h	25	54	56	54
Weight loss of the exposed specimens (%)	0.85	0.67	0.73	0.76

Table 4.34 Results of creep after 200 days [14]

Concrete mixture	Creep (10^{-6})		Stress (MPa)	Specific Creep (10^{-6}/MPa)		Drying creep (10^{-6}/MPa)
	Dry	Sealed		Dry	Sealed	
OPC	358	285	13.9	25.8	20.5	5.3
MK5	312	235	16.8	18.5	14.0	4.5
MK10	201	126	17.7	11.3	7.2	4.1
MK15	171	115	17.9	9.5	6.4	3.1

pozzolanic reaction of MK and its filler effect. The 200-day specific drying creep which is taken as the difference between the specific total creep and basic creep was also reduced for MK concretes.

Gleize et al. [27] investigated the effects of high-purity metakaolin (MK) on the autogenous shrinkage of pastes. Pastes were made with two water/binder ratios (0.3 and 0.5), and cement was partially replaced with 5, 10, 15 and 20% metakaolin. The MK was high-purity MK with a surface area of 23,000 m^2/kg and an average particle size of 4 µm. Figure 4.37 shows the autogenous shrinkage with time for pastes containing up to 20% MK, at water–solid ratios of 0.3 and 0.5. They concluded that (1) no overall expansion of pastes was observed at early ages; and (2) long-term autogenous shrinkage of cement–MK paste, with w/b ratios of 0.3 and 0.5, decreased with the increase in MK content.

Khatib [37] studied the length change of concrete containing metakaolin (MK) at a low water to binder ratio of 0.30. Portland cement (PC) was partially replaced

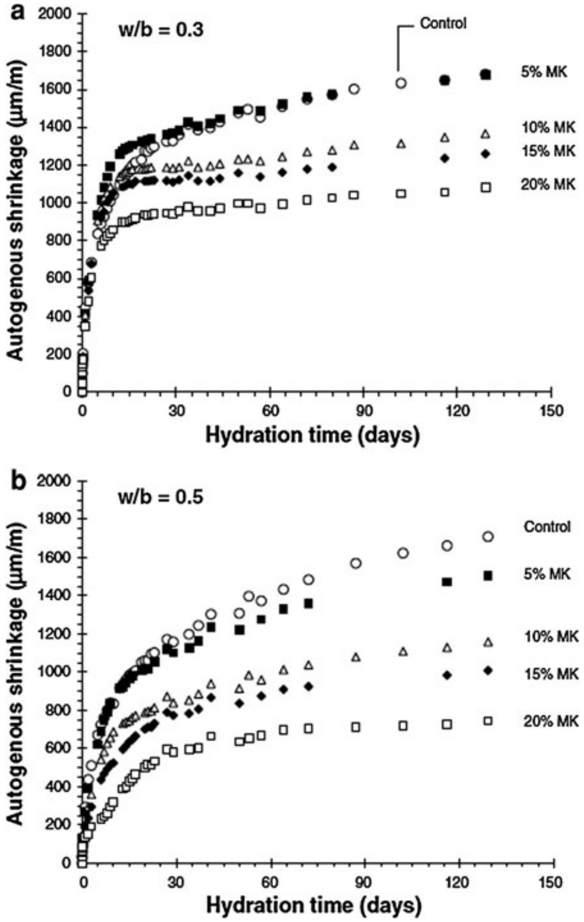


Fig. 4.37 Autogenous shrinkage of cement paste [27]

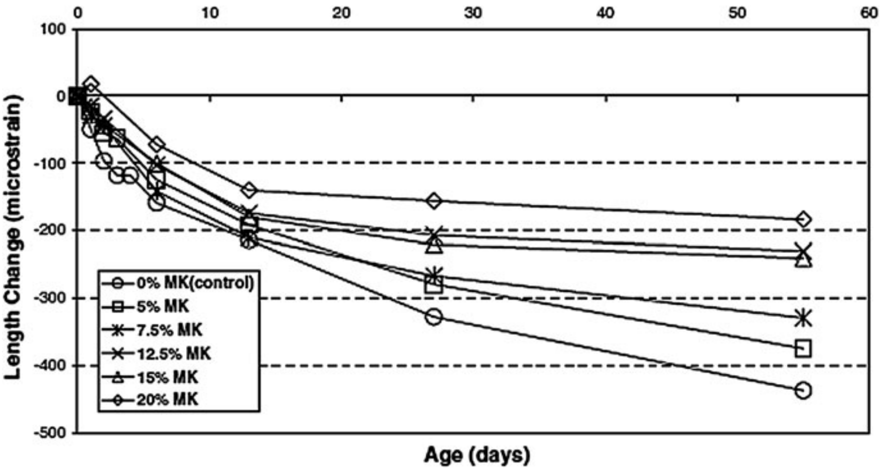


Fig. 4.38 Length change for MK concrete subjected to air curing at 20°C, 55% RH [37]

with 0–20% MK. Results of length change for MK concrete subjected to air curing at 20°C, 55% RH is shown in Fig. 4.38. There appeared to be systematic decrease in shrinkage as the MK content increases. Partial replacement of PC with 20% MK can reduce the long-term shrinkage by more than half compared with that of the control.

References

1. Al-Akhras, N.M.: Durability of metakaolin to sulfate attack. Cem. Concr. Res. **36**(9), 1727–1734 (2006)
2. Ambroise, J., Maximilien, S., Pera, J.: Properties of metakaolin blended cements. Adv. Cem. Based Mater. **1**(4), 161–168 (1994)
3. Aquino, W., Lange, D.A., Olek, D.A.: The influence of metakaolin and silica fume on the chemistry of alkali–silica reaction products. Cem. Concr. Compos. **23**(6), 485–493 (2001)
4. Asbridge, A.H., Walters, G.V., Jones, T.R.: Ternary blended concretes-OPC/GGBFS/metakaolin, pp. 547–557. Concrete across Borders, Denmark (1994)
5. Asbridge, A.H., Chadbourn, G.A., Page, C.L.: Effects of metakaolin and the interfacial transition zone on the diffusion of chloride ions through cement mortars. Cem. Concr. Res. **31**(11), 1567–1572 (2001)
6. Asbridge, A.H., Page, C.L., Page, M.M.: Effects of metakaolin, water/binder ratio and interfacial transition zones on the micro hardness of cement mortars. Cem. Concr. Res. **32**(9), 1365–1369 (2002)
7. ASTM C 618.: Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Concrete. Annual Book of ASTM Standards, Philadelphia (1993)
8. Badogiannis, E., Papadakis, V.G., Chaniotakis, E., Tsivilis, S.: Exploitation of poor Greek kaolins: strength development of metakaolin concrete and evaluation by means of k-value. Cem. Concr. Res. **34**(6), 1035–1041 (2004)

9. Badogiannis, E., Kakali, G., Dimopoulou, G., Chaniotakis, E., Tsivilis, S.: Metakaolin as a main cement constituent: exploitation of poor Greek kaolins. Cem. Concr. Compos. **27**(2), 197–203 (2005)
10. Badogiannis, E., Tsivilis, S.: Exploitation of poor Greek Kaolins: durability of metakaolin concrete. Cem. Concr. Compos. **31**(2), 128–133 (2009)
11. Batis, G., Pantazopoulou, P., Tsivilis, S., Badogiannis, E.: The effect of metakaolin on the corrosion behavior of cement mortars. Cem. Concr. Compos. **27**(1), 125–130 (2005)
12. Bredy, P., Chabannet, M., Pera, J.: Microstructural and porosity of metakaolin blended cements. Mater. Res. Soc. Symp. **137**, 431–436 (1989)
13. Boddy, A., Hooton, R.D., Gruber, K.A.: Long-term testing of the chloride-penetration resistance of concrete containing high-reactivity metakaolin. Cem. Concr. Res. **31**(5), 759–765 (2001)
14. Brooks, J.J., Johari, M.M.A.: Effect of metakaolin on creep and shrinkage of concrete. Cem. Concr. Compos. **23**(6), 495–502 (2001)
15. Cabrera, J., Rojas, M.F.: Mechanism of hydration of the metakaolin–lime–water system. Cem. Concr. Res. **31**(2), 177–182 (2001)
16. Cabrera, J.G., Nwaubani, S.O.: The microstructure and chloride ion diffusion characteristics of cements containing metakaolin and fly ash. In: V.M. Malhotra (ed.), Sixth CANMET/ACI/JCI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, vol. 1, pp. 385–400. Bangkok, Thailand (1998)
17. Cachim, P., Velosa, A.L., Rocha, F.: Effect of Portuguese metakaolin on hydraulic lime concrete using different curing conditions. Construct. Build. Mater. **24**(1), 71–78 (2010)
18. Caldarone, M.A., Gruber, K.A., Burg, R.G.: High reactivity metakaolin: a new generation mineral admixture. Concr. Int. **16**(11), 37–40 (1994)
19. Changling, H., Osbaeck, B., Makovicky, E.: Pozzolanic reaction of six principal clay minerals: activation reactivity assessments and technological effects. Cem. Concr. Res. **25**(8), 1691–1702 (1995)
20. Coleman, N.J., Page, C.L.: Aspects of the pore solution chemistry of hydrated cement pastes containing metakaolin. Cem. Concr. Res. **27**(1), 147–154 (1997)
21. Courard, L., Darimont, A., Schouterden, M., Ferauche, F., Willem, X., Degeimbre, R.: Durability of mortars modified with metakaolin. Cem. Concr. Res. **33**(9), 473–1479 (2003)
22. Curcio, F., Deangelis, B.A., Pagliolico, S.: Metakaolin as pozzolanic micro filler for high-performance mortars. Cem. Concr. Res. **28**(6), 803–809 (1998)
23. Dias, W.P.S.: Reduction of concrete sorptivity with age through carbonation. Cem. Concr. Res. **30**(8), 1255–1261 (2000)
24. Frías, M., Cabrera, J.: Pore size distribution and degree of hydration of MK–cement pastes. Cem. Concr. Res. **30**(4), 561–569 (2000)
25. Frías, M., Sánchez de Rojas, M.I., Cabrera, J.: The effect that the pozzolanic reaction of metakaolin has on the heat evolution in metakaolin–cement mortars. Cem. Concr. Res. **30**(2), 209–216 (2000)
26. Frías, M., Cabrera, J.: Influence of MK on the reaction kinetics in MK/lime and MK-blended cement systems at 20°C. Cem. Concr. Res. **31**(4), 519–527 (2001)
27. Gleize, F.J.P., Cyr, M., Escadeillas, G.: Effects of metakaolin on autogenous shrinkage of cement pastes. Cem. Concr. Compos. **29**(2), 80–87 (2007)
28. Gonçalves, J.P., Tavares, L.M., Filho, R.D.T., Fairbairn, E.M.R.: Performance evaluation of cement mortars modified with metakaolin or ground brick. Construct. Build. Mater. **23**(5), 1971–1979 (2009)
29. Gruber, K.A., Ramlochan, T., Boddy, A., Hooton, R.D., Thomas, M.D.A.: Increasing concrete durability with high-reactivity metakaolin. Cem. Concr. Res. **23**(6), 479–484 (2001)
30. Igurashi, S., Bentur, A., Mindess, S.: Micro-hardness testing of cementitious materials. Adv. Cem. Based Mater. **4**, 48–57 (1996)
31. Janotka, I., Puertas, F., Palacios, M., Kuliffayova, M., Varga, C.: Metakaolin sand-blended-cement pastes: rheology, hydration process and mechanical properties. Construct. Build. Mater. **24**(5), 791–802 (2010)

32. Jin, X., Li, Z.: Effects of mineral admixture on properties of young concrete. J. Mater. Civil Eng. **15**(5), 435–442 (2003)
33. Khatib, J.M., Mangat, P.S.: Absorption characteristics of concrete as a function of location relative to casting position. Cem. Concr. Res. **25**(5), 999–1010 (1995)
34. Khatib, J.M., Wild, S.: Pore size distribution of metakaolin paste. Cem. Concr. Res. **26**(10), 1545–1553 (1996)
35. Khatib, J.M., Wild, S.: Sulfate resistance of metakaolin mortar. Cem. Concr. Res. **28**(1), 83–92 (1998)
36. Khatib, J.M., Clay, R.M.: Absorption characteristics of metakaolin concrete. Cem. Concr. Res. **34**(1), 19–29 (2004)
37. Khatib, J.M.: Metakaolin concrete at a low water to binder ratio. Construct. Build. Mater. **22**(8), 1691–1700 (2008)
38. Kim, H.S., Lee, S.H., Moon, H.Y.: Strength properties and durability aspects of high strength concrete using Korean metakaolin. Construct. Build. Mater. **21**(6), 1229–1237 (2007)
39. Kinuthia, J.M., Wild, S., Sabir, B.B., Bai, J.: Self-compensating autogenous shrinkage in Portland cement–metakaolin-fly ash pastes. Adv. Cem. Res. **12**(1), 35–43 (2000)
40. Klimesch, D.S., Ray, A.: Autoclaved cement-quartz pastes with metakaolin additions. Adv. Cem. based Mater. **7**(3–4), 109–117 (1998)
41. Kostuch, J.A., Walters, G,V., Jones, T.R.: High performance concrete incorporating metakaolin—a review, pp. 1799–1811. Concrete 2000, University of Dundee (1993)
42. Lagier, F., Kurtis, K.E.: Influence of Portland cement composition on early age reactions with metakaolin. Cem. Concr. Res. **37**(10), 1411–1417 (2007)
43. Larbi, J.A., Bijen, J.M.: Influence of pozzolans on the Portland cement paste–aggregate interface in relation to diffusion of ions and water absorption in concrete. Cem. Concr. Res. **22**, 551–562 (1992)
44. Lee, S.T., Moon, H.Y., Hooton, R.D., Kim, J.P.: Effect of solution concentrations and replacement levels of metakaolin on the resistance of mortars exposed to magnesium sulfate solutions. Cem. Concr. Res. **35**(7), 1314–1323 (2005)
45. Li, Z., Ding, Z.: Property improvement of Portland cement by incorporating with metakaolin and slag. Cem. Concr. Res. **33**(4), 579–584 (2003)
46. Lyubimova, T.Y., Pinus, E.R.: Crystallization structure in the contact zone between aggregate and Cem.. Concr. Kolloidn. Z. (USSR) **24**(5), 578–587 (1962)
47. Murat, M.: Hydration reaction and hardening of calcined clays and related mineral-I Preliminary investigations on metakaolin. Cem. Concr. Res. **13**(2), 259–266 (1983)
48. Oriol, M., Pera, J.: Pozzolanic activity of metakaolin under microwave treatment. Cem. Concr. Res. **25**(2), 265–270 (1995)
49. Poon, C.S., Lam, L., Kou, S.C., Wong, Y.L., Wong, R.: Rate of pozzolanic reaction of metakaolin in high-performance Cem. pastes. Cem. Concr. Res. **31**(9), 1301–1306 (2001)
50. Poon, C.S., Azhar, S., Anson, M., Wong, Y.L.: Performance of metakaolin concrete at elevated temperatures. Cem. Concr. Compos. **25**(1), 83–89 (2003)
51. Poon, C.S., Kou, S.C., Lam, L.: Compressive strength, chloride diffusivity and pore structure of high performance metakaolin and silica fume concrete. Construct. Build. Mater. **20**(10), 858–865 (2006)
52. Potgieter-Vermaak, S.S., Potgieter, J.H.: Metakaolin as an extender in South African cement. J. Mater. Civil Eng. **18**(4), 619–623 (2006)
53. Qian, X., Li, Z.: The relationships between stress and strain for high-performance concrete with metakaolin. Cem. Concr. Res. **31**(11), 1607–1611 (2001)
54. Ramlochan, T., Thomas, M., Gruber, K.A.: The effect of metakaolin on alkali–silica reaction in concrete. Cem. Concr. Res. **30**(3), 339–344 (2000)
55. Razak, H.A., Chai, H.K., Wong, H.S.: Near surface characteristics of concrete containing supplementary cementing materials. Cem. Concr. Compos. **26**(7), 883–889 (2004)
56. Rojas, M.F., Cabrera, J.: The effect of temperature on the hydration rate and stability of the hydration phases of metakaolin–lime–water systems. Cem. Concr. Res. **32**(1), 133–138 (2002)

57. Rojas, M.F., Sánchez de Rojas, M.I.: The effect of high curing temperature on the reaction kinetics in MK/lime and MK-blended cement matrices at 60°C. Cem. Concr. Res. **33**(5), 643–649 (2003)
58. Rojas, M.F.: Study of hydrated phases present in a MK–lime system cured at 60°C and 60 months of reaction. Cem. Concr. Res. **36**(5), 827–831 (2006)
59. Roy, D.M., Arjunan, P., Silsbee, M.R.: Effect of silica fume, metakaolin, and low-calcium fly ash on chemical resistance of concrete. Cem. Concr. Res. **31**(12), 1809–1813 (2001)
60. Saito, M., Kawamura, M.: Resistance of the cement–aggregate interfacial zone to the propagation of cracks. Cem. Concr. Res. **16**(5), 653–661 (1986)
61. Salvador, S.: Pozzolanic properties of flash-calcined kaolinite: a comparative study with soak-calcined products. Cem. Concr. Res. **25**(1), 102–112 (1995)
62. Sha, W., Pereira, G.B.: Differential scanning calorimetry study of ordinary Portland cement paste containing metakaolin and theoretical approach of metakaolin activity. Cem. Concr. Compos. **23**(6), 455–461 (2001)
63. Shvarzman, A., Kovler, K., Grader, G.S., Shter, G.E.: The effect of dehydroxylation/ amorphization degree on pozzolanic activity of kaolinite. Cem. Concr. Res. **33**(3), 405–416 (2003)
64. Sun, W., Zhang, Y.-S., Lin, W., Liu, Z.-Y.: In situ monitoring of the hydration process of K-PS geopolymer cement with ESEM. Cem. Concr. Res. **34**(6), 935–940 (2004)
65. Tafraoui, A., Escadeillas, G., Lebaili, S., Vidal, T.: Metakaolin in the formulation of UHPC. Construct. Build. Mater. **23**(2), 669–674 (2009)
66. Thomas, M.D.A., Gruber, K.A., Hooton, R.D.: The use of high reactivity metakaolin in high performance concrete. 1st Engineering Foundation Conference on High Strength Concrete, Hawaii **1997**, 517–530 (1997)
67. Wild, S., Khatib, J.M., Jones, A.: Relative strength, pozzolanic activity and cement hydration in superplasticised metakaolin concrete. Cem. Concr. Res. **26**(10), 1537–1544 (1996)
68. Wild, S., Khatib, J.M.: Portlandite Consumption in metakaolin cement pastes and mortars. Cem. Concr. Res. **27**(1), 137–146 (1997)
69. Wild, S., Khatib, J., Roose, J.L.: Chemical and autogenous shrinkage of Portland cement–metakaolin pastes. Adv. Cem. Res. **10**(3), 109–119 (1998)
70. Wong, H.S., Razak, H.A.: Efficiency of calcined kaolin and silica fume as cement replacement material for strength performance. Cem. Concr. Res. **35**(4), 696–702 (2005)
71. Zhang, M.H., Malhotra, V.M.: Characteristics of a thermally activated alumino-silicate pozzolanic material and its use in concrete. Cem. Concr. Res. **25**(8), 1713–1725 (1995)