

Chapter 5

Metakaolin

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Abstract Metakaolin (MK) is known to be a highly pozzolanic material that can be used in concrete. MK is usually produced by heating kaolin-containing clays, within the temperature range of about 600–900 °C. This chapter summarizes the utilization of metakaolin in relevant worldwide standards, mainly in Europe and North America. The health, safety and environmental sustainability concerns on using metakaolin as a supplementary cementitious material are also addressed in this chapter. It is reported that MK incorporation has benefits on both early-age and long-term properties. On the other hand, this chapter also reports that the results of heat of hydration and rate of reaction in metakaolin-blended concrete are controversial and need further investigation. Overall, the optimum level of cement replacement by MK is around 10–20%, which provides concrete the maximum strength. Metakaolin appears to have an excellent potential as a supplementary

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N. De Belie et al. (eds.), *Properties of Fresh and Hardened Concrete Containing
Supplementary Cementitious Materials*, RILEM State-of-the-Art Reports 25,
https://doi.org/10.1007/978-3-319-70606-1_5

cementitious material in structures made of high-performance concrete, because it controls deleterious expansion due to alkali-silica reaction in concrete (depending on the nature of the aggregate), and reduces the ingress of chloride by improving the microstructure and chloride binding behavior.

Keywords Metakaolin · High-performance concrete · Supplementary cementitious material · Properties · Sustainability

5.1 Overview and Background

To reduce the environmental impact of the global cement industry, and to achieve cost and performance benefits in concrete production, metakaolin (MK) and other supplementary cementitious materials are used as partial replacements for cement in concrete. Metakaolin reacts chemically via a pozzolanic process with $\text{Ca}(\text{OH})_2$, as a source of reactive Si and Al, and its degree of structural disorder plays a major role in determining its reactivity (Shvarzman et al. 2003).

Sabir et al. (2001) carried out a review of the utilization of metakaolin as a pozzolanic material for mortar and concrete and reported that the use of metakaolin as a pozzolan will help in the development of early strength and also give some improvement in long term strength. Metakaolin addition alters the pore structure in cement paste, mortar and concrete, and greatly improves its resistance to transport of water and diffusion of harmful ions, which can lead to the degradation of the matrix, as will be discussed in detail later in this chapter. Siddique and Klaus (2009) also reviewed the use of MK as a partial replacement for cement in mortar and concrete, producing results which are in general agreement with those of Sabir et al. (2001): MK was found to be an effective pozzolan in concrete, enhancing both the early age and long-term mechanical performance, reducing the water penetration into concrete by capillary action, reducing permeability, improving the resistance to sulfate attack, increasing chemical resistance, and offering control of deleterious expansion due to alkali-silica reaction. These properties, and others, will be addressed in this chapter.

Kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, (shown in Fig. 5.1) is a clay mineral that provides the basis of the plasticity of traditional ceramics in the unfired (hydrous) state; it can be converted by firing to produce a hard, durable, watertight, water-resistant material, which has for millennia been used in everyday life worldwide. The name of kaolin is derived from the Chinese term ‘Kao-ling’ meaning high ridge, the name of a hill in the city of Jingdezhen, where this material was mined centuries ago for use in ceramic production. Structurally, kaolinite consists of octahedral alumina sheets and tetrahedral silica sheets stacked alternately, and takes on a plate-like morphology as shown in Fig. 5.2.

The typical microstructure observed is shown in Fig. 5.3.

Metakaolin, which has the approximate chemical formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ or AS_2 , is produced by heating kaolin-containing clays within the temperature range of

Fig. 5.1 Kaolin (Rashad 2013)



Fig. 5.2 Kaolin plates and stacks (Murray 2000)



about 600–900 °C. Kaolinite crystals with hexagonal morphology tend to be preserved when heating kaolin at a temperature of 550 °C. Heating kaolin above 550 °C transforms it into MK by the loss of structural OH groups and a rearrangement in Si and Al atoms leading to a decrease in octahedral Al and the appearance of penta- and tetra-coordinated Al (Brown et al. 1985). As the temperature increases (650 and 800 °C), the kaolinite flakes become more deformed and locally condensed into disordered material, although the original layered structure of the kaolinite is at least partially retained (White et al. 2010a, b; Lee et al. 1999, 2001). Above 900–950 °C, MK begins to recrystallize to a siliceous spinel and disordered silica; at higher temperatures, crystalline mullite is generated (Brown et al. 1985). The spinel and mullite phases both have low pozzolanic

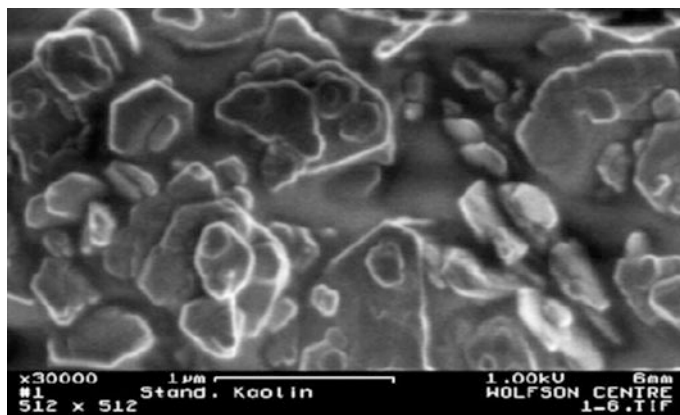


Fig. 5.3 HR-SEM micrograph of pure standard kaolin Shvarzman et al. (2003)

activity, and sintering also takes place, so the over-calcination of MK reduces its reactivity as a supplementary cementitious material.

In the pure form, disordered kaolins tend to yield metakaolin with higher pozzolanic activity (Kakali et al. 2001), and it has also been suggested that chemical treatment to introduce additional stacking faults into a high-crystallinity kaolin may provide a more highly reactive material (White et al. 2011). The calcination conditions need to be selected and optimized for each type of kaolin to provide optimal reactivity (Shvarzman et al. 2003), as the dehydroxylation of kaolinite during calcination is known to be a complex, multi-step, kinetically-controlled process (Bellotto et al. 1995; Lee et al. 1999; MacKenzie et al. 1985; White et al. 2010b). This process is also complicated by impurities in the clays, where the processing conditions may need to be altered to optimize the removal of sulfates (Badogiannis et al. 2005b) or to account for the presence of a larger volume of unreactive components such as quartz (Castillo et al. 2010), or less-reactive non-kaolin type clays (He et al. 1995; Habert et al. 2009).

According to Shvarzman et al. (2003), the dehydroxylation of kaolinite is preceded by a “pre-dehydroxylation” stage in the range 80–150 °C where the evolution of a small amount of water is observed, see Fig. 5.4a. Between 900 and 1100 °C, the exothermic formation of crystalline phases such as spinel and mullite is characterized by an exothermic peak in the DTA curve and insignificant weight loss in the TGA curve, see Fig. 5.4b. It is also noted that the commercial calcination of kaolinite, whether carried out via traditional rotary kiln processes or the increasingly-popular flash calcination process, often does not result in full dehydroxylation of the clay particles, and a non-zero loss on ignition is thus observed (San Nicolas et al. 2013, 2014).

Rashad (2013) presented a comprehensive overview of the previous works carried out on kaolin history, MK sources, production and composition. Based on the comparison of different thermal treatment, which includes calcination

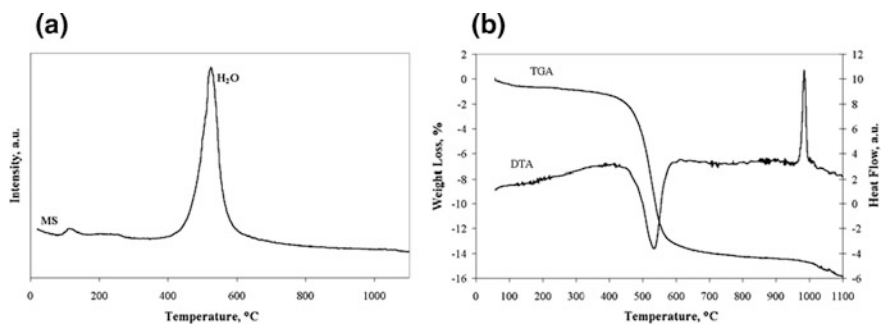


Fig. 5.4 **a** Mass spectroscopy analysis of water released by pure kaolinite during calcination; **b** DTA and TGA curves for pure kaolinite (Shvarzman et al. 2003)

Table 5.1 Typical chemical composition of a metakaolin (Ambroise et al. 1994)

| Component | % by weight |
|--------------------------------|-------------|
| SiO ₂ | 51.5 |
| Al ₂ O ₃ | 40.2 |
| Fe ₂ O ₃ | 1.2 |
| CaO | 2.0 |
| MgO | 0.1 |
| K ₂ O | 0.5 |
| SO ₃ | 0.0 |
| TiO ₂ | 2.3 |
| Na ₂ O | 0.1 |
| L.O.I. | 2.0 |

temperatures and heating periods, he concluded that the optimum temperature for heating kaolin to obtain MK may be in the range from 600 to 850 °C for 1–12 h.

The typical chemical composition of metakaolin as reported by Ambroise et al. (1994) is given in Table 5.1. Commercial sources of kaolin are rarely 100% pure kaolinite, often containing silica (quartz) impurities, as well as some substitution of Fe³⁺ for Al³⁺ in the octahedral layers. The ceramics industry generally demands higher purity (and thus ‘whiteness’) of the clay than is required for use as a pozzolan, but commercial exploitation of clay deposits tends to focus on those of higher purity and thus higher value, as it is currently motivated more by demand from the higher-value-added ceramics industry, with the production of cementitious components a secondary consideration for many producers.

There are also alternative sources of materials which can be used in place of pure calcined kaolinite clay. These include:

- Lower purity kaolin clays containing moderate to high amounts of quartz can be used as pozzolans (Castillo et al. 2010)
- Paper sludge—this is often a mixture of kaolin with cellulose, sometimes also containing calcite, which can be calcined to give an impure metakaolin-like material (Banfill and Frias 2007)

- 2:1 layered clays such as illite and montmorillonite can be used, but tend to show lower pozzolanic activity, and thermal processes for their amorphization are less effective than for kaolinite (Snellings et al. 2012)
- The 1:1 tubular clay halloysite is not yet widely studied in PC blends, but is known to be moderately reactive in alkali-activation (MacKenzie 2009), and so may offer scope for utilisation in place of metakaolin in the parts of the world where it is available.

5.2 List of Relevant Standards

Blends of Portland cement (PC) with up to 30% metakaolin are fairly widely tested, and are incorporated into the European standard for common cements (EN 197-1: 2011) (European Committee for Standardization (CEN) 2011) in two categories: CEM II/A-Q, 6–20% metakaolin, and CEM II/B-Q, 21–35% metakaolin. Metakaolin can also be included in Portland-composite cements (CEM II/A-M and CEM II/B-M), and in potentially higher fractions in the CEM IV and CEM V specifications in parallel with another SCM. The main limitations on the achievable degree of metakaolin inclusion in many concretes are related to the water demand of this material, related to its plate-like particle morphology, as well as its very high specific surface area, which is far higher than that of fly ash, and almost approaching that of silica fume considered as the finest SCM, see Table 5.2.

In Europe (except France) metakaolin is not among the materials whose general suitability as a Type II (at-mixer pozzolanic or latent hydraulic) addition is incorporated into EN 206: 2013 (European Committee for Standardization (CEN) 2013), and so no k -value has been defined in that standard for metakaolin. Since 2012 in France, the national complement of NF EN 206/CN (Association Française de Normalisation (AFNOR) 2014) allows the use of up to 15% MK for all exposure classes of concrete, with a k -value of 1. The requirements for MK are found in the French standard NF P18-513 (Association Française de Normalisation (AFNOR) 2012), entirely dedicated to the specifications of MK. The main requirement is the need of an activity index of 1 at 28 days (based on a substitution level of 15 wt%). Other requirements include chemical characteristics of the metakaolin (e.g., $\text{Al}_2\text{O}_3 + \text{SiO}_2 > 90$ wt%), and calcium hydroxide fixation (Chapelle modified test)

Table 5.2 Specific surface area of kaolin and metakaolin measured by BET (N_2 adsorption-desorption at 77 K, Monosorb, Quantachrome) method (Ambrose et al. 1994), in comparison with that of fly ash and silica fume

| SCM | Specific surface area, m^2/kg |
|-------------|---|
| Metakaolin | 12–15 |
| Kaolin | 16–18 |
| Fly ash | 2.3 |
| Silica fume | 18.0 |

of at least 700 mg $\text{Ca(OH)}_2/\text{g}$ of metakaolin. Moreover, two categories of fineness and water demand are defined to characterize the metakaolin.

In the North American regime, metakaolin is classified by ASTM C 618 (ASTM International 2015b) as a Class N material, acceptable as long as it does not increase the water requirement of the cement by more than 15% (among other stipulated properties), and so ASTM C 595 (ASTM International 2015a) allows its use in blended cements at replacement levels of up to 40%. The American Concrete Institute has also reported on the use and application of metakaolin in concrete via a report (ACI Committee 232 2012), including commentary on the technical rationale underpinning the ASTM standards in this area. Similarly, metakaolin is described in Canadian standard A3001-08 (Canadian Standards Association 2008a) as a Type N material, while requirements of primary properties are aligned with ASTM. A3004-E1 (Canadian Standards Association 2008b) represents a practical evaluation of alternative SCMs which do not meet current definitions of SCMs in A3001-08 (Canadian Standards Association 2008a).

Metakaolin is not included as a possible cement component in Australian Standard AS 3972-2010 (Standards Australia 2010). Indian Standard IS 456: 2000 includes metakaolin as an allowed mineral admixture, with the properties of the metakaolin itself governed by the recently-approved IS 16354 (Bureau of Indian Standards 2015). Brazilian Standard NBR 5736: 1991 (Associação Brasileira de Normas Técnicas 1999) describes pozzolanic cements with replacement levels of Portland cement by pozzolans (including metakaolin) of up to 50% as cements of class CP-IV.

5.3 Health and Safety Issues

Metakaolin appears to be exempt from the REACH legislation (EC Regulation 2006) under Annex V.7, as a mineral that has not been chemically modified (*definition: Not chemically modified substance: means a substance whose chemical structure remains unchanged, even if it has undergone a chemical process or treatment, or a physical mineralogical transformation, for instance to remove impurities*). Little information is available regarding the leaching of any potentially hazardous elements from the metakaolin itself. Cr^{6+} seems to be found only in very small quantities in commercial MK (<1 ppm) (San Nicolas 2011). It would be expected that any leaching would differ very significantly between materials from different clay deposits, and so this absence of hazard will need to be validated on a local level rather than by making general assumptions. Metakaolin is often used in blended cements to decrease the leaching of nuclear or toxic wastes. Pera and Bonnin (1996) showed that the use of 20% of metakaolin led to a reduction in the heavy metals leached into the mixing water from pastes and mortars containing solutions of chromium, lead and cadmium. Metakaolin was used by Cyr et al. (2012) in ternary and quaternary binders using cement (75 wt%), metakaolin (22.5 wt%), and industrial by-products from combustion processes containing

heavy metals. Results showed that the use of metakaolin led to a significant decrease in soluble fractions and heavy metals like Cr, Cd, As, Cu or Pb.

The key concern related to most commercial metakaolins would be associated with respirable crystalline silica, which is a minor component of a high-reactivity metakaolin but is present at much more significant levels in less-pure products, and requires appropriate precautions and personal protective equipment to be employed.

5.4 Environmental Sustainability

Kaolinite clays are widely available worldwide, and have been identified as potentially providing a low-cost, high-volume source of SCMs, if some technical issues related to the physicochemical nature of the metakaolin particles can be overcome. Because metakaolin is not generally sourced as an industrial by-product, its supply is much more future-proof than most commonly used supplementary cementitious materials. Industries such as coal-fired electricity generation and ironmaking are likely to see significant structural and technological changes in coming decades—either led by the industries or imposed by regulators—which means that the supply and characteristics of the by-products derived from these processes are likely to be affected. Conversely, metakaolin is a direct manufactured mineral product, relying only on the availability of (globally widely distributed) kaolin-type clay deposits, moderate-temperature calcination, and grinding facilities.

If cement is to be partially substituted by metakaolin, the following ecological aspects play an important role: the production process itself, and the transport to the site of utilization, see Fig. 5.5.

Specifically:

1. **Transport distance** from the production place of the metakaolin to the place where the concrete is produced needs to be taken into account. The transport distance is sometimes not transparent through the cost price, because the ex-factory prices are highly different. Relevant metakaolin production in Europe takes place in France, Great Britain, Germany, Czech Republic, Ukraine and Bulgaria, among others. There are also commercially known metakaolins

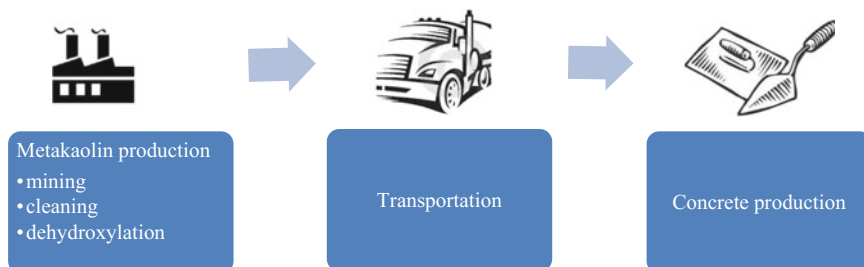


Fig. 5.5 Steps involved in the utilization of metakaolin

produced in the USA, Brazil, Canada, China and India. The transport history cannot be neglected and should be investigated by the supplier. Long transport distances might turn a positive eco-balance into a less favorable situation.

2. The production process itself: how much ecological impact is made during the production process of the metakaolin. The production process can be separated into the activities of mining and cleaning steps to reach a certain kaolinite quality, and as third step the transformation to metakaolin during a heat treatment at about 500–900 °C. Within the mining step several activities might be necessary such as breaking/milling and drying of the raw kaolin source. Extensive cleaning steps might be necessary if the resource contains low amounts of kaolinite and/or a very pure or white material has to be produced. These activities have consequences for the environmental impact, for instance in the energy demand and pollution of the environment due to cleaning chemicals. The dehydroxylation to obtain highly reactive metakaolin takes place either in a rotary kiln, a shaft kiln, fluidized bed furnace, flash calciner or a pulsation furnace. Due to the different efficiencies of these thermal processes and the amount and type of fuels used, the energy demand (CED—cumulative energy demand) as well as the CO₂ emissions [GWP 100—global warming potential (GWP)] might be very different between processes. Reliable and verified data about the environmental impact are difficult to obtain, but Table 5.3 summarizes some of the data which have been collated. The main differences are related to whether the kaolin is originally produced with a high purity or not, see columns 2–4 in comparison to columns 5–7. Further, the furnace and fuel type seem also to play an important role (Table 5.3).

For a plausibility check, two other processes might be considered. The GWP given in the ECOINVENT database (<http://www.ecoinvent.org/>) for comparable processes are:

- The whole process of producing natural anhydrite is specified with 0.085 kg CO₂ eq./kg anhydrite. This natural material is produced by surface mining and further crushing, drying and milling. No further burning process is required.
- Production of expanded clay is specified with 0.3 kg CO₂ eq./kg. For this process also the clay is obtained from a surface mine, and the material is further crushed, dried and milled. The clay powder is afterwards granulated and burned in a rotary kiln at about 900 °C. Usually gas, oil or coal is used as fuel.

With this background, the data given can be evaluated as follows:

- A GWP below 0.1–0.2 kg CO₂ eq./kg metakaolin seems to be very ambitious, and probably only feasible with renewable fuel and usage of a very efficient furnace type such as a flash calciner.
- A GWP between 0.2 and 0.7 kg CO₂ eq./kg metakaolin seems to be a conservative basis for comparison with CEM I.
- Transport distances must be considered, especially if cement from nearby manufacturers is to be substituted by metakaolin purchased far away. For quick evaluation of the breakeven point, a GWP of 0.154–0.185 kg CO₂ eq./t km may be used.

Table 5.3 Environmental assessments of different metakaolins by comparison to CEM I cement

| Source | Weil et al. (2010) | Weil et al. (2010) | Weil et al. (2010) | Habert et al. (2011) | ARGECO (2013) | CEM I |
|---------------------------------|-----------------------|--------------------|---------------------|-----------------------|-----------------------|-----------|
| Product/area | EU | EU | Brazil | France | France | EU mean |
| GWP (kg CO ₂ eq./kg) | 0.67 | 0.52 | 0.57 | 0.09 | 0.09–0.2 | 0.8–1 |
| ARC ^a (kg Sb eq./kg) | 5.32 | 4.03 | 4.54 | 0.00017 | – | 1.5 |
| CED (MJ/kg) | 12.41 | 9.52 | 10.3 | – | 2.1–2.4 | 3.8–4.2 |
| Data source | Producer ^a | Different | Different | Different | Producer ^b | Ecoinvent |
| Mining | Producer ^c | Ecoinvent | Brazil ^d | Ecoinvent | | |
| Cleaning | Producer ^c | Ecoinvent | No | No | No | |
| | Intense ^e | | | | | |
| Burning | Producer ^c | | | Producer ^f | | |
| Furnace | Rotary kiln | | | | Flash calciner | |
| Fuel | Gas/oil | | | Biomass | Oil | |

^aData from a producer in Europe

^bARGECO (<http://www.argeco.fr/>), producer of ARGICEM/F (flash calcined), calculation made by LCPC

^cAbiotic resource consumption

^dSurface mine, transported by ship to Europe for further burning

^eKaolin produced for paper industry

^fAGS Mineraux/Imerys Group

5.5 Fresh Properties

5.5.1 Workability, Slump, Water Demand, Rheology, Bleeding

In terms of the influence of metakaolin on concrete rheology, the results described in the literature are very mixed (Hassan et al. 2010). In general, the workability of concrete containing metakaolin seems to be slightly poorer than plain Portland cement concrete, but less problematic (creamier and less sticky) than when silica fume is included. Processes such as flash calcination seem to produce, in addition to plate-like particles, some spherical particles similar to those obtained for fly ashes (Claverie et al. 2015). San Nicolas et al. (2013) found up to 20% of these spherical particles in MK, which improve the workability of the mixtures when compared to MK produced in rotary kiln (composed of only plate-like particles).

There is also a tendency towards higher thixotropy (Quanji 2010), which is probably related to the particle shape of the platy clay particles. For this, and other reasons, the agglomeration/dispersion state of the metakaolin powder seems to be important in determining the early-age properties of the concrete. Metakaolin addition may also reduce bleed of concrete (Andriolo and Sgarboza 1986).

Moulin et al. (2001) evaluated the rheology of metakaolin-blended pastes using a shear vane rheometer to characterize yield stress, and found that the presence of MK significantly increased both the 5 and 90-min yield stress when compared to reference pastes. This confirmed that MK blending results in a higher water demand and leads to thixotropic behavior, which was explained to be linked to the accelerating effect of MK on PC hydration.

Wild et al. (1996) reported that workability of concrete at 0.45 water cement (w/c) decreased with increase in replacement of cement by metakaolin. It is found that slump loss was in the range of 2–32 mm when replacement level of cement was in the range of 5–35%. Dubey and Banthia (1998) reported that on inclusion of 10% metakaolin, slump loss of 20 mm was observed as compared to control concrete. Qian and Li (2001) reported that for concrete with 1% superplasticizer addition, the slump progressively decreased with increasing metakaolin content. Comparable results showing reductions in slump or fluidity have been observed by other authors (Brooks and Johari 2001; Li and Ding 2003).

Bucher et al. (2015b) assessed the relevance of the use of metakaolin in self-compacting concretes (SCC) by using it as sole supplementary cementing material. Although the water demand of MK was higher, it was shown that this material could be used in SCC with the condition of using a suitable method of design that took into account the specific surface area of MK.

5.5.2 *Chemical Admixture Interaction*

Due to its sometimes-detrimental influence on rheology and its high surface area, the addition of metakaolin to concrete can lead to a higher demand for superplasticizers (San Nicolas et al. 2013). There also appears to be an increase in the demand for air-entraining agents (or a reduction in their efficiency) with metakaolin addition (Christodoulou 2000), but there is little openly available information in this regard. The balance between cement, metakaolin and gypsum is also challenging with regard to early-age behavior, and has been identified as particularly needing attention in ternary systems also containing limestone (Antoni et al. 2012).

5.5.3 *Setting Times, Plastic Settlement, Plastic Shrinkage, Curing*

Previous researchers have found MK incorporation to have varying effects on the setting behavior of mortars and pastes. The comparison of setting times depends significantly on whether mixes are designed to standard consistency (in which case the metakaolin-containing mixes have similar setting times to a PC control), or at constant w/cm —water to cementitious materials ratio (which yields a much shorter setting time in the metakaolin-containing mixes due to the high water demand of

metakaolin) (Justice et al. 2005). Problems in the determination of early-age properties by standard test methods have also been noted due to the dry nature of mixes at lower w/c ratios (Sabir et al. 2001). Brooks et al. (2000) examined the effect of silica fume, MK, FA, and slag on setting time of high strength concrete (HSC) via ASTM C403. For HSC containing MK, there was a progressive increase in the retarding effect up to 10% replacement, but a reduction at higher replacement levels.

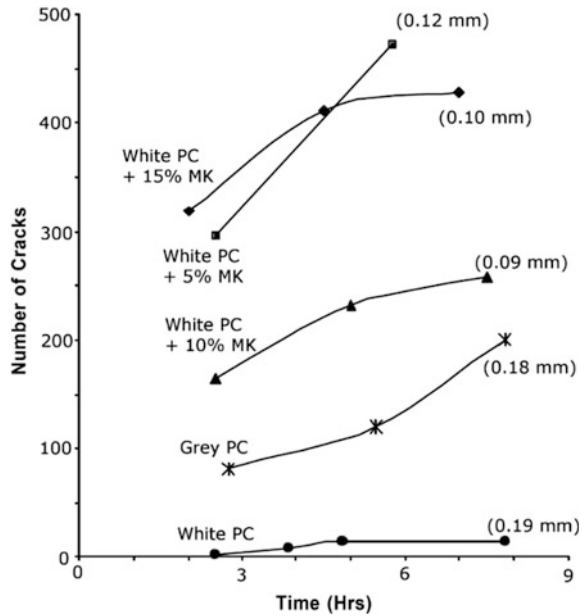
Similar results were reported by Batis et al. (2005) who examined both a commercially available MK product and local Greek kaolin heat-treated in their own lab, and found all MK mixtures to have significantly longer setting times than control pastes at normal consistency. The mixture with 20% MK set slowest, requiring 205 min for initial set compared to 105 min for the control. However, while the control mix required a w/cm of 0.275 to achieve normal consistency, 20% MK mixtures required a w/cm of 0.41. Vu et al. (2001) reported that for the particular Vietnamese kaolin used, setting times of pastes at normal consistency in the lower replacement range (10–20% MK) were not significantly affected by blending. Beyond this range, the initial and final setting times increased by 15 and 10%, respectively, attributed to the lower cement and higher water contents involved.

Badogiannis et al. (2005a) reported the water demand and setting times of cements containing five metakaolins, see Table 5.4. The amorphous contents in metakaolins MK1, MK2, MK3, and MK4 (derived from poor Greek kaolins) were 36, 37, 71, and 49% respectively, but 95% in a commercial metakaolin (denoted MKC) of high purity. The authors concluded that (1) blended cements demanded significantly more water than the unmodified cement; and (2) the initial and final setting time of metakaolin cements were affected by the metakaolin content. Cements with 10% metakaolin generally exhibited similar setting times to that of PC, while for 20% metakaolin content there was a delay in setting. MK4 showed the greatest effect on the setting time, as well as the highest water demand, see Table 5.4.

Table 5.4 Properties of metakaolin blended cements (Badogiannis et al. 2005a)

| Sample | Metakaolin (% mass) | Water demand (% mass) | Setting time | |
|--------|---------------------|-----------------------|--------------|-------|
| | | | 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 |

Fig. 5.6 Count of plastic shrinkage cracks on the surface of $610 \times 915 \times 19$ mm slabs of concretes exposed to moving air conditions at early age, for different percentages of replacement with MK. Values in parentheses are the average crack widths at 8 h for each specimen (Marikunte et al. 2004)



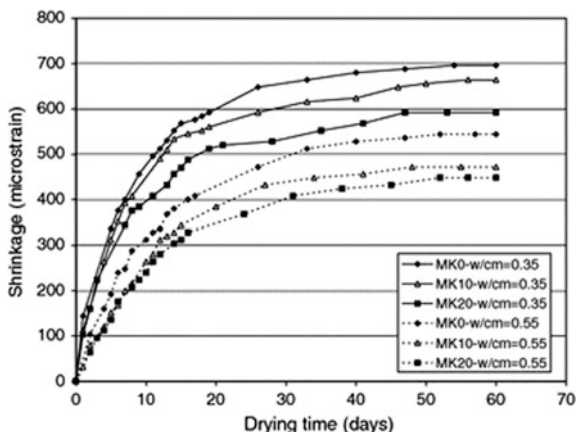
Cracking due to plastic settlement has been observed to be much higher in metakaolin-containing concretes than in control PC mixes (Marikunte et al. 2004), although the widths of the cracks appeared slightly narrower in specimens containing MK than in the unmodified samples, see Fig. 5.6.

5.6 Properties at Early Age

5.6.1 Autogenous Shrinkage

Metakaolin is known to be very effective in reducing autogenous shrinkage at later age (Gleize et al. 2007). Wild et al. (1998) investigated chemical shrinkage and swelling of MK-PC pastes with 5–25% MK, at a water/binder ratio of 0.55, for up to 45 days. Chemical shrinkage was also found to reach a maximum between 10 and 15% MK and then decrease sharply for higher MK contents. At later age in metakaolin-containing concretes, autogenous shrinkage appears to be reduced compared to PC alone (Gleize et al. 2007), and drying shrinkage also tends to be lower than that of PC, see Fig. 5.7, as long as the samples are cured appropriately before testing (Güneyisi et al. 2008, 2012), but seems to be less than PC-silica fume systems.

Fig. 5.7 Drying shrinkage of MK-blended concretes at 10 and 20% replacement levels, and w/c ratios of 0.35 and 0.55, from (Güneyisi et al. 2008)



5.6.2 Early Age Strength Development

The influence of MK on the early-age strength of concretes depends strongly on its particle size (i.e., reactive surface area), and also whether the comparison is conducted at constant w/c or at constant consistency. High fineness metakaolins can enhance early strength, less fine metakaolins sometimes have little influence on early strength and can sometimes reduce it, particularly at higher blending fractions. Sets of samples prepared at constant consistency will generally require more water in the MK-blended materials, as noted above, and this will have a negative influence on mechanical performance.

The reactivity of MK generally takes effect after a few days, so poor short-term performance can sometimes be obtained, which is a disadvantage in cases where the concrete needs to be rapidly stripped of its formwork. The use of chemical activators such as sodium sulfate is an efficient method to increase the short-term strength, but it could lead to a decreased activity at later ages (Saidat et al. 2012). Strength evolution as a function of curing duration will be considered in more detail later in the chapter.

5.6.3 Heat of Hydration, Rate of Reaction (Influence of Temperature and Curing, Maturity Functions)

Results available in the literature related to reaction rates and heat output are very mixed, largely because of the differences between the characteristics of various metakaolins as noted in the previous section. Some reports show a higher overall heat of hydration of blended cements containing metakaolin, others show similar or slightly lower, but few authors account in detail for the filler effect and corresponding acceleration of PC hydration in these discussions. The potential role of

metakaolin in chemically accelerating PC hydration has also been suggested but requires further investigation (Ambroise et al. 1994; Wild and Khatib 1997). There seems to be a tendency towards increased heat release beyond the first few days due to the pozzolanic reaction (Frías et al. 2000), but the point at which the heat evolution exceeds that of plain PC seems to depend mainly on the fineness of the metakaolin, which is both (a) variable, and (b) rarely reported accurately. So, it becomes difficult to draw overall conclusions regarding the influence of metakaolin on early-age heat evolution.

According to Zhang and Malhotra (1995), 10% replacement of PC with MK caused a 7 °C increase in the early-age temperature rise compared to PC concrete. Ambroise et al. (1994) reported temperature rises of 8, 6 and 1 °C over controls, for 10, 20 and 30% replacement, respectively, in mortars. The smaller temperature increases at higher replacement levels are likely to be due to the dilution effect of removing such a large mass of Portland cement from the system. By comparison, replacement with 10% silica fume produced a temperature rise of only 0.5 °C in the same study.

Bai and Wild (2002) looked specifically at the effects of FA and MK on heat evolved from insulated 150 mm cube mortar specimens, see Fig. 5.8. With increasing replacement levels, the temperature rise in FA systems was found to decrease, while the temperature rise in MK systems increased substantially. Ternary blends at total PC replacement levels of up to 40% appeared to have a compensatory effect on temperature rise: the temperature rise for a 10% FA-10% MK blend was the same as that of the control, see Fig. 5.8b.

Figure 5.9 shows the time to peak temperature for the binary and ternary blend mortars. Both FA and MK delay the time taken to reach peak temperature. The time delay imparted by MK, see Fig. 5.9a, is, however, greater than that imparted by FA at the same replacement level and, unlike FA, MK does not produce systematic changes in delay time with an increase in the replacement level. When both FA and MK are blended together with PC, see Fig. 5.9b, the delay time may increase substantially with an increase in the proportion of MK to FA in the blend. At 30 and

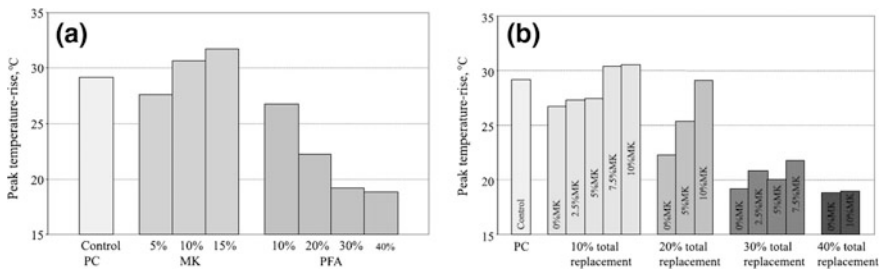


Fig. 5.8 **a** Peak temperature rise for metakaolin and FA blended PC mortars; **b** Peak temperature rise for PC-MK-FA blended mortars, as a function of the total replacement level and the fraction of this that is MK (Bai and Wild 2002)

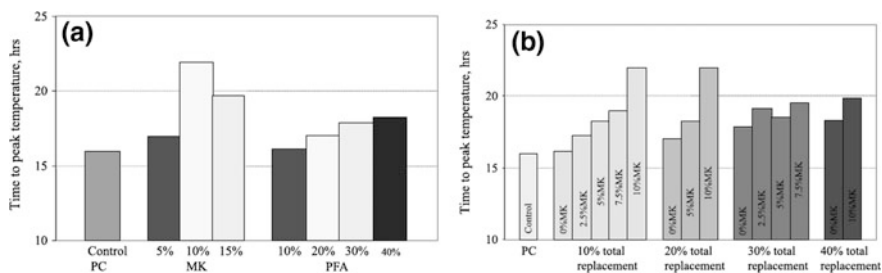


Fig. 5.9 **a** Time to peak temperature for metakaolin and FA blended mortars; **b** Time to peak temperature for MK-FA-PC blended mortars as a function of the total replacement level and the fraction of this that is MK (Bai and Wild 2002)

40% total replacement levels, the observed impact of the MK on the delay time was less pronounced because of the much lower MK to FA ratios employed in these mixtures.

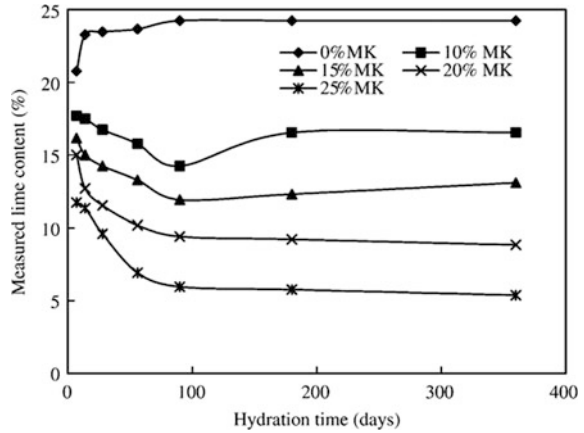
The principal reaction of metakaolin during cement hydration is between the MK (represented here as AS_2) and the CH derived from cement hydration, in the presence of water. This reaction forms additional cementitious C-A-S-H gel, together with crystalline products, which include calcium aluminate hydrates and aluminosilicate hydrates (C_2ASH_8 , C_4AH_{13} and C_3AH_6). The crystalline products depend principally on the AS_2/CH ratio and the reaction temperature.

Kostuch et al. (2000) reported that the CH content of hydrated cement paste was significantly reduced during the time of the reaction for MK replacement levels of 10 and 20%; 20% replacement of cement by MK led to consumption of all of the CH at 28 days. Oriol and Pera (1995) reported that between 30 and 40% MK was required to remove all the CH from an MK-PC paste at a water binder ratio of 0.5 when cured in lime-saturated water for 28 days. Ambroise et al. (1994) showed that during the hydration period, CH was quickly consumed, the microstructure was rich in C-S-H and strätlingite (C_2ASH_8), and the pore size distribution was refined. At up to 30% replacement, MK acted as an accelerating agent, and the CH content was considerably reduced.

Frias and Cabrera (2000) determined the degree of hydration of MK-PC pastes according to the measured CH content at a w/c ratio of 0.55 as a function of blending fraction and age, see Fig. 5.10. Calcium hydroxide contents of MK/PC samples increased with age until 3–7 days as the PC hydrated. Subsequently, the values started decreasing, at a time that depends on the MK content. In the cases of mixtures with 10 and 15% MK, an inflection point at 56 and 90 days, respectively, was observed and corresponded to the consumption of the CH by MK in the pozzolanic reaction, and beyond this point, the calcium hydroxide content progressively increased.

The pozzolanic reaction of metakaolin could be promoted by microwave heating (Oriol and Pera 1995). As heat is generated quickly inside the cementitious material, thermal acceleration of the reaction becomes more efficient, allowing both

Fig. 5.10 Calcium hydroxide content as a function of time in pastes at $w/c = 0.55$ and with different levels of replacement of PC by MK, as marked (Frias and Cabrera 2000)



reduction of the necessary amount of metakaolin (15% instead of 30–40% in normal conditions) and of the w/c ratio (0.4 instead of 0.5). These results are quite interesting for the development of fiber-reinforced cement composites, in which microwave heating allows the reduction of the curing period.

5.7 Compressive Strength

Many researchers have found that compressive strength of concrete produced with metakaolin increased when compared to control mixtures, for instance Wild et al. (1996) reported that a maximum increase of 35% in 28-day strength was identified at a 20% replacement level. Higher surface area metakaolins generally yield a higher strength and the fastest rate of strength gain. Dubey and Banthia (1998) reported that upon inclusion of 10% high reactivity (high purity and fineness) metakaolin, compressive strength increased by 9% at 28 days. Qian and Li (2001) also reported that the compressive strength increases substantially with metakaolin addition; at 3 days, an increase of 51% in concrete strength was achieved at 15% MK relative to concrete without metakaolin. The 3 day strength achieved at 15% MK was higher than the 28 day strength without metakaolin, confirming that metakaolin has a pronounced influence on early strength. Li and Ding (2003) also showed that the ternary combination of MK with PC and ultra-fine slag provided higher strength gains at 28 days than were achieved in the absence of slag.

As with other SCMs, the mechanical efficiency of MK is strongly dependent on the characteristics of the cement used. A statistical analysis done on a set of 11 different PC (Cyr et al. 2014) showed a good correlation of compressive strength of MK mixes with the contents of C_3A , C_4AF and SO_3 of PC. On the other hand, the fineness of cements, and their C_3S , C_2S , and Na_2O_{eq} contents were not correlated.

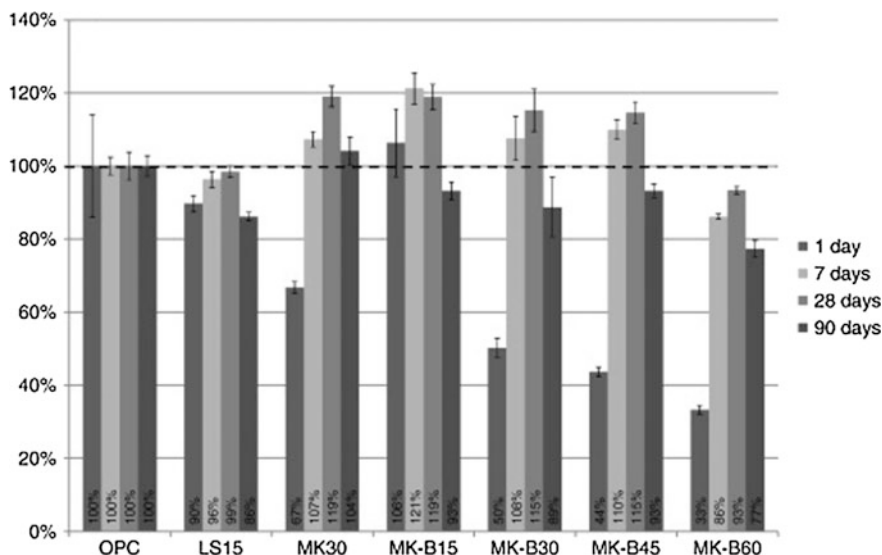


Fig. 5.11 Relative compressive strengths of Portland cement blends with various percentages (as marked) of limestone (LS), metakaolin (MK), and a 2:1 blend of the two (MK-B); data from (Antoni et al. 2012), all values are presented as a percentage of the Portland cement control specimen at the same age

In particular, the pozzolanic reaction was postponed with low- C_3A cements compared to normal Portland cement.

The combination of metakaolin with limestone at high substitution percentages, both with (Bernal et al. 2011) and without (Antoni et al. 2012) an added alkali source, has also recently been noted to give improved binder properties related to the formation of carboaluminates, strätlingite, and other Al-rich binding phases which contribute to the strength, see Fig. 5.11, and impermeability of the material.

5.8 Tensile Strength

The tensile strength of concrete incorporating metakaolin shows similar tendencies to those observed in concretes without metakaolin; there does not appear to be strong evidence for modifying the standard calculation processes whereby tensile strength is predicted from compressive strength by power-law relationships (Lawler et al. 2007). Any metakaolin addition that improves compressive strength, as outlined in section 10, would therefore be expected to correspondingly enhance tensile strength also. For example, Qian and Li (2001) reported that the tensile and compressive strengths of concrete both increase systematically with increasing metakaolin replacement level up to 15%, as shown in Table 5.5.

Table 5.5 Tensile and compressive strengths of concrete with different replacement levels of Portland cement by metakaolin (Qian and Li 2001)

| Metakaolin content (% mass) | | | | |
|-----------------------------|------|------|------|------|
| Strength at 28 d | 0 | 5 | 10 | 15 |
| Direct tensile | 3.35 | 3.58 | 3.88 | 4.29 |
| Compressive | 37.8 | 45.7 | 63.8 | 69.7 |

5.9 Flexural Strength

The comments presented earlier for tensile strength are also relevant for discussion of flexural strength; it is highly likely that the improvements in compressive strength that are achieved by addition of metakaolin will induce corresponding improvements in flexural strength. For example, Dubey and Banthia (1998) reported that on inclusion of 10% metakaolin, flexural strength increased by 9% at 28 days; the flexural toughness factor for concrete containing metakaolin was about 9% greater than for nonpozzolanic control concrete and 21% greater than for the silica fume concrete in the same study. Justice and Kurtis (2007) also reported that flexural strength measured in 4-point loading of concrete specimens was increased by 20–40% at 8% metakaolin addition.

5.10 Modulus of Elasticity

As it has been shown to increase compressive strength and to densify the microstructure, it follows that the addition of MK might also lead to increased modulus of elasticity (MOE), yielding a stiffer or more brittle concrete. From the literature, MOE generally seems to increase with increasing MK content, although the rate of increase is lower than that observed for compressive strength.

Qian and Li (2001) reported that after three days of curing, concrete containing 15% MK had an elastic modulus of 26.2 GPa, compared to 24.1 GPa for the control sample at this age. At 60 days of age, 15% MK and control concretes showed modulus values of 34.7 and 30.4 GPa, respectively. Those authors also commented on the notable increase in the brittle behaviour of the metakaolin concretes during mechanical testing. Khatib and Hibbert (2005) evaluated dynamic modulus of elasticity for $w/c = 0.50$ concretes containing 0, 10, or 20% MK. They found that MK increased the modulus values at all curing times, but that there was little difference observed between 10 and 20% MK replacement. Between 28 and 90 days in the metakaolin, the dynamic modulus of elasticity increased from 38 to 50 GPa, indicating significant ongoing reaction of the MK beyond 28 days. Justice and Kurtis (2007) reported that by inclusion of 8% metakaolin, an increase in elastic modulus by 5–19% compared to control concrete was observed.

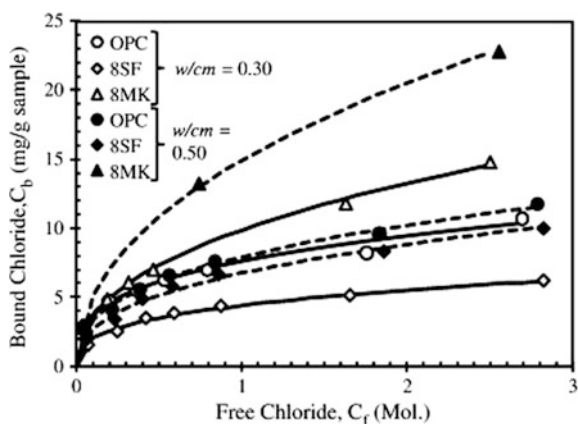
5.11 Fatigue

Based on the results of static and fatigue flexural tests conducted by Kaur et al. (2014), it is revealed that the addition of MK (and also of silica fume and fly ash) enhances the mechanical behaviour of fiber-reinforced concretes, probably through densification of the paste and interfacial transition zone microstructures (as identified in other studies, e.g., (Duan et al. 2013), analysing microhardness). However, metakaolin was only tested under fatigue conditions as a component of ternary blends so it is difficult to isolate its effects from those of the other blending components (fly ash and limestone powder). There are very few data available in the literature regarding the influence of metakaolin on fatigue performance of concrete, so this is an area that would benefit from further study.

5.12 Transport Properties and Related Durability Issues

Metakaolin is well known to contribute to the technical properties of concretes with regard to pore refinement leading to lower permeability (Ambroise et al. 1994; Frías and Cabrera 2000; Poon et al. 2006; Ramezani-pour and Bahrami Jovein 2012). However, this depends to some extent on the testing method adopted for analysis of porosity and permeability, and also in some cases on the curing duration prior to testing (Courard et al. 2003; Frías and Cabrera 2000; Khatib and Clay 2004). The additional aluminate phases formed through the pozzolanic reaction of metakaolin can also aid in resistance to chloride penetration through chemical binding effects, see Fig. 5.12, specifically the conversion of AFm phases to Friedel's salt (Thomas et al. 2012), and can also reduce alkali-silica expansion (Ramlochan et al. 2000). However, the carbonation rates of concretes containing MK may be either better or worse than those of plain PC—there is a trade-off between binder chemistry (where

Fig. 5.12 Chloride binding isotherms of pastes with 8% replacement of PC by either silica fume or metakaolin, at w/c ratios of 0.30 and 0.50 (Thomas et al. 2012)



lower calcium content tends to give higher carbonation rates) and permeability (which is normally reduced by metakaolin addition). The carbonation depths of mixtures of MK and PC (up to 25%) are similar to the ones of commercially blended cements containing fly ash or GGBS (e.g., CEM III/A and CEM V/A) (Bucher et al. 2015a). Combination of MK and limestone filler could be an interesting way to reduce the carbonation of MK blended cements (Bucher et al. 2015a), as the hemicarboaluminates formed in these ternary mixtures (Antoni et al. 2012) tend to be transformed into calcite when the CO₂ concentration increases (Damidot et al. 1994), meaning that these hydrates could play the role (as Portlandite) of CO₂ pump in clinker-limestone filler-MK mixtures (Bucher et al. 2015a).

The influence of MK in improving concrete durability is achieved to a significant degree in the interfacial transition zone (ITZ), which is characterized by a higher local w/c, a higher porosity, and differing mineralogical and chemical composition than the bulk paste. These properties of the ITZ can be detrimental to transport-related durability properties, in particular resistance to chloride and sulfate transport. MK has shown an effect on the chemistry and microstructure of the ITZ, and may thus play a significant role in reducing ion diffusion and improving concrete durability (Asbridge et al. 2001).

PC-MK concretes show significantly lower conductivity values than PC concrete (Zhang and Malhotra 1995), which is often taken as an indication of good resistance to chloride ingress. Courard et al. (2003) examined the chloride diffusion rates of mortars which contained 0, 10, 15, and 20% metakaolin as partial replacement of cement using a non-steady state through-diffusion test. The apparent diffusion coefficient of the mortar rose with 5% MK addition but then decreased with metakaolin content from 5 to 15%, see Table 5.6; however, the mortar with 20% MK did not show breakthrough of chlorides through a 7 mm thick specimen even after 300 days.

Khatib and Wild (1998) evaluated the effect of metakaolin on the sulfate resistance of blended cement mortars. Expansion was found to decrease systematically with an increase in MK content (from 5 to 20%), for two cements having high C₃A and intermediate C₃A levels. Mortars containing high C₃A cement and 0–10% MK showed rapid expansion and deterioration between 40 and 70 days of exposure to a 5% sodium sulfate solution, while those with 15 or 20% MK showed a small but rapid expansion during this time period, but subsequently stabilized and

Table 5.6 Chloride diffusion rates for mortars with CEM I 42.5, metakaolin and kaolin (Courard et al. 2003)

| 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 | >300 d | – |

contracted slightly. For the intermediate-C₃A cement mortars, the expansion process was delayed significantly. Those containing 10% or more MK exhibited essentially no expansion, while those containing 0 or 5% did not begin expanding until 150 days and did not grow rapidly until approximately 350 days. Al-Akhras (2006) also showed an improvement in resistance to sodium sulfate attack, even at w/c ratios as high as 0.6.

However, Lee et al. (2005) found that metakaolin influences negatively the performance of mortar or paste specimens when exposed to magnesium sulfate solution. This is partially attributed to the formation of gypsum, but not ettringite and thaumasite. Another possible reason may be the decalcification of primary and secondary C-S-H gel following the formation of M-S-H gel.

In terms of alkali-silica reaction (ASR), Ramlochan et al. (2000) reported that incorporation of metakaolin as a partial cement replacement at levels between 10 and 15% may be sufficient to mitigate deleterious expansion from ASR in concrete, depending on the nature of the aggregate. The mechanism by which metakaolin may suppress expansion due to alkali-silica reaction appeared to be entrapment of alkalis by the supplementary hydrates and a consequent decrease in the pH of pore solutions.

Zhang and Malhotra (1995) evaluated the performance of air-entrained concretes incorporating metakaolin in ASTM C 666 (ASTM International 2015c) freeze-thaw tests and in ASTM C 672 (ASTM International, 2012) salt scaling tests. Concrete with 10% metakaolin showed great resistance to freeze-thaw damage, with a residual flexural strength of 89% and a durability factor of 100.3%, after 300 cycles of freezing and thawing. On the other hand, the residual flexural strength and durability factor values for the control Portland cement concrete specimens were 85 and 98.3% respectively. For the salt-scaling test, the concrete incorporating 10% metakaolin underperformed slightly when compared to the control concrete, but had similar results to the concrete with 10% SF.

Badogiannis and Tsvivilis (2009) prepared nine concrete mixtures: a reference PC concrete and eight metakaolin concretes where metakaolin replaced either cement or sand in percentages 10 or 20% by weight of the control cement content. The metakaolin concrete, compared to PC concrete, exhibited significantly lower chloride permeability, gas permeability and sorptivity because of refinement of the pore structure of the metakaolin mixtures.

Batis et al. (2005) prepared eight mortar mixtures: a reference PC concrete and six metakaolin mortars where metakaolin replaced either cement or sand in percentages 10 or 20% by weight of the control cement content. They measured the corrosion resistance of prepared mortars against chloride and carbonation induced corrosion. They concluded that the use of metakaolin, either as a sand replacement up to 20% weight of the control cement content, or as a cement replacement up to 10%, improved the corrosion behavior of mortar specimens. However, higher percentages of metakaolin decreased the corrosion resistance.

San Nicolas et al. (2014) applied the concept of equivalent performance by assessing the durability of concrete using metakaolin as a Portland cement replacement. The study considered large panels of concrete types, with different

workabilities, from immediate release to self-compacting concrete, and different strengths from low to high performance concrete, for either general or structural purpose. Many technical benefits for the concrete user, such as lower permeability, higher strength and decreased chloride ion penetration were found. It seemed from that study that MK met the requirements of the equivalent performance concept.

5.13 Concluding Remarks

Metakaolin can be considered as a highly pozzolanic material and appears to have an excellent potential as a supplementary cementing material for high-performance cementitious materials. However, there are a number of characteristics of metakaolin-blended concrete, which need additional detailed analysis to aid in the deployment of this material as a large-scale supplementary cementitious material:

- Sulfate resistance depends on metakaolin content and the method of measurement (strength or expansion) (Khatib and Wild 1998)
- Shrinkage behaviour seems variable and needs further analysis
- Effect of clay source/mineralogy is complex—this is currently understood mainly on an empirical level, but theoretical developments are now moving rapidly
- Other long-term mechanical properties, e.g., creep of concrete, require additional investigation
- Molecular level details of interactions with organics are not yet well described.

The optimum level of cement replacement seems to be around 10–20%, where maximum strength is observed. Incorporation of high reactivity metakaolin as a partial cement replacement between 10 and 15% may also be sufficient to control deleterious expansion due to alkali-silica reaction in concrete, depending on the nature of the aggregate. The addition of metakaolin reduces the ingress of chloride by improving the microstructure and chloride binding behaviour.

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