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Metakaolin and calcined clays as pozzolans for concrete: a review

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Abstract

The utilisation of calcined clay, in the form of metakaolin (MK), as a pozzolanic material for mortar and concrete has received considerable attention in recent years. This interest is part of the widely spread attention directed towards the utilisation of wastes and industrial by-products in order to minimise Portland cement (PC) consumption, the manufacture of which being environmentally damaging. Another reason is that mortar and concrete, which contain pozzolanic materials, exhibit considerable enhancement in durability properties. This paper reviews work carried out on the use of MK as a partial pozzolanic replacement for cement in mortar and concrete and in the containment of hazardous wastes. The literature demonstrates that MK is an effective pozzolan which causes great improvement in the pore structure and hence the resistance of the concrete to the action of harmful solutions. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Metakaolin; Calcined clays; Concrete

1. Introduction

Concrete is probably the most extensively used construction material in the world. It is only second to water as the most heavily consumed substance with about six billion tonnes being produced every year. This is largely due to the abundance of raw materials for cement manufacture, low relative cost and the versatility and adaptability of concrete in forming various structural shapes. However, environmental concerns both in terms of damage caused by the extraction of raw material and CO_2 emission during cement manufacture have brought about pressures to reduce cement consumption by the use of supplementary materials. These materials may be naturally occurring, industrial wastes or by-products or those that require relatively less energy to manufacture. Other concerns that have contributed to these pressures are related to the increase in the number of incidents where concrete structures have experienced serious deterioration.

In addressing these concerns and other environmental problems relating to the disposal of waste industrial by-products and also because of economic advantages, mixtures of Portland cement (PC) and pozzolans are now very commonly used in concrete production [1].

Originally the term pozzolana was associated with naturally formed volcanic ashes and calcined earths, which react with lime at ambient temperatures in the presence of water. In recent times the term has been extended to cover all siliceous/aluminous materials which, in finely divided form and in the presence of water, will react chemically with calcium hydroxide (CH) to form compounds that possess cementitious properties. This generalised definition covers waste products such as fly ash (FA), rice husk ash and silica fume (SF). The utilisation of pozzolans results in added technical advantages manifested in reductions in temperature rise and improvements in durability and strength enhancement, although in some cases strength develops more slowly.

PC, if fully hydrated, produces CH of about 28% of its own weight, although in practice, in fully mature concrete, this figure would not normally exceed 20%. The CH (Portlandite) reacts with the added pozzolan resulting in additional calcium silicate hydrates. The CH liberated by the hydration of PC does not make a significant contribution to strength and can be harmful to concrete durability. Its elimination or reduction by reaction with the pozzolan can result in greatly enhanced durability and strength. Because of these technical advantages and in some cases economic advantages there has, over the last few decades, been increasing and widespread utilisation of FA, SF and natural zeolite in concrete. This trend is currently

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receiving much greater impetus because of the distinct environmental benefits.

The volume of industrial by-products, with pozzolanic properties, produced world-wide exceeds their current utilisation, and it is widely believed [2] that their utilisation will increase with increasing realisation of the environmental benefits associated with such use. This will contribute to the requirements of environmental protection and sustainable construction in the future [1].

There are therefore compelling reasons, in the long-term, to extend the practice of partially replacing cement in concrete and mortar with waste and other less energy intensive processed materials, which have pozzolanic properties. One possible source for a pozzolan is calcined clay. Natural pozzolans in the form of calcined earths blended with lime have been used to produce cementitious materials for thousands of years [3,4]. Structures such as water tanks, aqueducts, walls and bridges 4000 years old have been constructed from thermally activated clay and lime mortars [5,6]. The Romans, in addition to their discovery [7] that volcanic ash deposits in Pozzuoli combined with lime and water to produce a strong cementing material, used crushed tiles as a pozzolan [8], particularly in regions such as Britain where volcanic ash was not available. For example, the masonry of Hadrians wall, built between 122 and 130 AD to divide Scotland from England, is bonded by mortar comprising lime, crushed tile, crushed sandstone, sand, and kiln debris [9]. The potential of utilising waste clay bricks as a pozzolanic partial cement replacement material for mortar and concrete has been examined in a recent study by the authors in collaboration with other establishments in Europe [10].

The utilisation of calcined clay in the form of metakaolin (MK) as a pozzolanic addition for mortar and concrete has received considerable interest in recent years. Much of this interest has focused on removal of the CH, which is produced by the hydration of cement and which is associated with poor durability. CH removal has a major influence on resistance to sulphate attack and alkali silica reaction (ASR), and also provides enhanced strength, which is derived from the additional cementitious phases generated by reaction of CH with MK. MK is processed from high-purity kaolin clay by calcination at moderate temperatures (650–800°C). It contains silica and alumina in an active form which will react with the CH. The principal reasons for the use of clay-based pozzolans in mortar and concrete have been materials availability and durability enhancement. In addition, depending on the calcining temperature and clay type, it is also possible to obtain enhancement in strength, particularly during the early stages of curing. The very early strength enhancement is due to a combination of the filler effect and accelerated cement hydration [46].Subsequently, these effects are enhanced by the pozzolanic reaction between MK and the CH produced by the hydration of the cement. The benefits of using pozzolanic materials are manifest not only in the many examples of ancient constructions that still exist today, e.g., the Pantheon in Rome built in 127 AD, but also in more recent constructions. An example of the latter is the construction of a reservoir in the Amazon basin, where, in the 1960s, approximately 300,000 tonnes of locally produced calcined clays were blended with more costly imported PC. It was reported [11] that these structures did not suffer from ASR despite the fact that highly reactive aggregate was used. ASR resistance was attributed to the incorporation of the calcined clay in the concrete. This paper reviews the research carried out on the use of MK as a pozzolanic partial cement replacement material for mortar and concrete and in applications of containment of hazardous wastes and other pollutants.

2. The pozzolanic reaction

The calcination conditions of kaolinite and the characterisation of MK have been the subject of research since the latter part of the 19th century. An extensive survey on this subject in the context of the ceramic industry is given by Brindley and Nakahira [12–14].

It is known [15,16] that thermal activation in air (at 600–900°C) of many clay mineral leads, by dehydroxylation, to breakdown or partial breakdown of the crystal lattice structure forming a transition phase with high reactivity. A typical example is the production of metakaolinite ($Al_2O_3 \cdot 2SiO_2$) or AS_2 by calcining clay or lateritic soils [17] rich in kaolinite. The chemical reactions involved when calcined clays are used as pozzolans for concrete have been discussed by Malquori [18] and Turrizani [19] and more recently by DeSilva et al. [20] and Dunster et al. [21]. The principal reaction is that between the AS_2 and the CH derived from cement hydration, in the presence of water. This reaction forms additional, cementitious aluminium containing CSH gel, together with crystalline products, which include calcium aluminate hydrates and alumino-silicate hydrates (i.e., C_2ASH_8, C_4AH_{13} and C_3AH_6). The crystalline products formed depend principally on the AS_2/CH ratio and the reaction temperature [22–25].In addition if carbonate is freely available carbo-aluminates may also be produced. The optimum replacement levels of PC by MK are associated with changes in the nature and proportion of the different reaction products (depending on composition) temperature and reaction time, which are formed in the PC–MK system.

Several studies [26–29] have been conducted to examine the hydration reaction and to determine the level of reactivity of MK in terms of the processing conditions and the purity of the 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 [29]. The thermal activation temperature, which is generally in the range 700–800°C, is of critical importance and depends on the base mineral used. These studies showed that increasing compressive strengths and decreasing levels of CH in hardened concrete are obtained with feed clays that are rich in kaolin (90%). By determining the reactivity level using the Chapelle test, MK processed under appropriate conditions has been found [29,30] to be a very efficient pozzolan. Table 1 compares the reactivity of MK, expressed as consumption rates of CH per gram of pozzolan, to those of SF and FA. Clearly these values will vary with respect to the quality of the pozzolan. The data presented in Table 1 should, however, be viewed with caution as the Chapelle test is performed at elevated temperature and provides no information regarding reaction rate at ambient temperatures. The amount of CH in cured concrete can be measured by thermogravimetric analysis (TG) and differential thermal analysis (DTA) [31]. In addition, the reactivity of the pozzolan can be assessed by chemical determination of unreacted pozzolan in hydrated PC-pozzolan pastes [32]. The pozzolanic activity of MK has also been assessed by comparing the heat evolution of MK–PC mortars with SF–PC and FA–PC mortars [33]. The results showed that during the first 24 h of hydration, MK–PC mortars, similarly to SF–PC mortars, showed slightly increased heat evolution relative to PC mortars. In contrast, FA–PC mortars showed a significantly reduced heat output.

Fig. 1 (after Kostuch et al. [29]) gives the variation in the CH content in concrete blended with MK with curing time. It is seen that the CH is significantly reduced at all curing times and for both replacement levels. Reports on the amount of MK required to fully remove the CH vary. Kostuch et al.'s [29] results show that 20% replacement of cement by MK is required to remove all the CH in concrete at 28 days, whereas Oriol et al. [34] report that between 30% and 40% MK is required to remove all the CH in MK–PC paste at a w/b ratio of 0.5 when cured in lime-saturated water for 28 days. These variations are not surprising as the products of hydration and pozzolanic activity depend to large extents on the PC composition, the purity of the MK and the w/b ratio. Also the CH in concrete is present in a much more dilute state than in paste and is more difficult to quantify.

Table 1
Pozzolanic activity of various pozzolans [30]

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

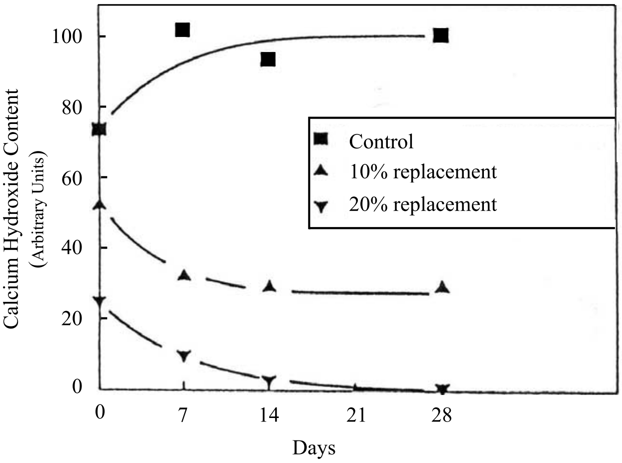

Fig. 1. Effect of MK replacement level on the CH content of concrete as it cures [29].

3. Calcining temperature

The burning or calcining temperature of clay affects the pozzolanic reactivity of the resulting product. The clay is in its most reactive state when the calcining temperature leads to loss of hydroxyls and results in a collapsed and disarranged clay structure. The calcining temperature producing the active state is usually in the range 600–800°C [16]. Ambroise et al. [26] determined the effect of the calcining temperature of kaolinite (600–800°C) on the strength development of 1:1 MK-lime pastes of water:solids ratio 0.72, at different curing times. The optimum calcining temperature, to give maximum strength at 3, 7 and 28 days was 700°C. In another paper, Ambroise et al. [27] showed that calcination below 700°C results in less reactive metakaolinite with more residual kaolinite. Above 850°C crystallisation occurs and reactivity declines. Marwan et al. [35] have shown that on calcination at 800°C kaolinite and gibbsite present in lateritic soils are transformed into transition phases of MK and amorphous alumina. If clays are heated at even higher calcining temperatures liquid phase forms which on cooling solidifies into an amorphous glass phase. Amorphous glass also shows pozzolanic activity as in the case of FAs, which are normally composed of 70–90% glass phase.

Kaolinites are usually calcined in rotary kilns or using fluidised bed processes which allows the reduction of calcining time from hours to minutes. Salvador and Davies [36,37] used flash-calcination to reduce the calcining time to seconds. The process consists of rapid heating, calcining and cooling. The authors showed that different qualities of MK are obtained depending on the temperature (500–1000°C) and time of flash-calcination (0.5–12 s) and that more active MK can be produced by this method, than by soaking.

4. Portlandite consumption

Wild and Khatib [38] determined the CH consumption and strength development in MK–PC pastes and mortars, which were cured in water at 20°C. MK was employed as partial PC replacements of 0, 5, 10 and 15%. The CH contents at the various stages of curing (up to 365 days) were determined by TG analysis and the results are reproduced in Fig. 2. The CH, expressed as a percentage of PC, in MK mortars and their equivalent neat pastes showed a minimum at about 14 days of curing. This was attributed to a peak in pozzolanic activity for which more CH is being removed from the paste by reaction with MK, than is being generated by the cement hydration. At an age of one year there is still a substantial amount of CH remaining, even for paste with 15% replacement of PC by MK, which suggests replacement levels considerably in excess of 15% are required to fully consume all the CH produced. The required level of PC replacement will also depend on the purity of MK and the quantity of CH produced by the PC, which is determined by the PC composition and water/cement ratio.

Fig. 3 gives the relative compressive strength developments in the mortars and the pastes examined in [38]. Relative strength is defined as the ratio of the strength at a given age to the strength of the control mortar or paste without MK at the same age. The peak in relative compressive strength at 14 days coincided with a maximum in pozzolanic activity (Fig. 2) and represents an increase in compressive strength, above those of the control, of 40%. Enhancement in compressive strength was obtained at all ages and for all substitution levels.

Oriol and Pera [34] examined the level of lime consumption in MK blended cement pastes under microwave curing conditions using infrared spectrometry. The authors reported that total elimination of lime (CH) is achievable in binders containing 15% MK. They also reported that between 30% and 40% of MK is required to remove all the CH in PC–MK paste with a water/binder (w/b) ratio of 0.5 when cured in lime-saturated water at room temperature for 28 days. The binder is the total of all cementitious materials used.

Wild et al. [39] showed that increasing the specific surface of MK from 12,000 to $15,000\ \mathrm{m^2/kg}$ reduces the age at which maximum strength enhancement occurs in MK mortar. The increase in the specific surface of the MK did not influence the long-term (90-day) strength. This increase in fineness also resulted in an increase in the optimum level of replacement of cement by MK.

Curcio et al. [40] examined the strength development in mortars containing 15% MK as partial PC replacement by weight. Their results for mortars containing MKs, which differed in origin and fineness, and SF are shown in Fig. 4. Their superplasticised mortars ($w/b = 0.33$) gave compressive strengths similar to, and in some cases, greater than SF mixtures. When examined in terms of relative strength, the results show that all the MK concretes give peaks in pozzolanic activity at curing times below 28 days.

5. Pore refinement

The influence of MK on the microstructure and diffusion properties of blended cement pastes and concrete have been studied by Kostuch et al [29], Bredy et al. [41] and Khatib and Wild [42]. The pore size distribution for the mortars examined in [29] are shown in Fig. 5. It is

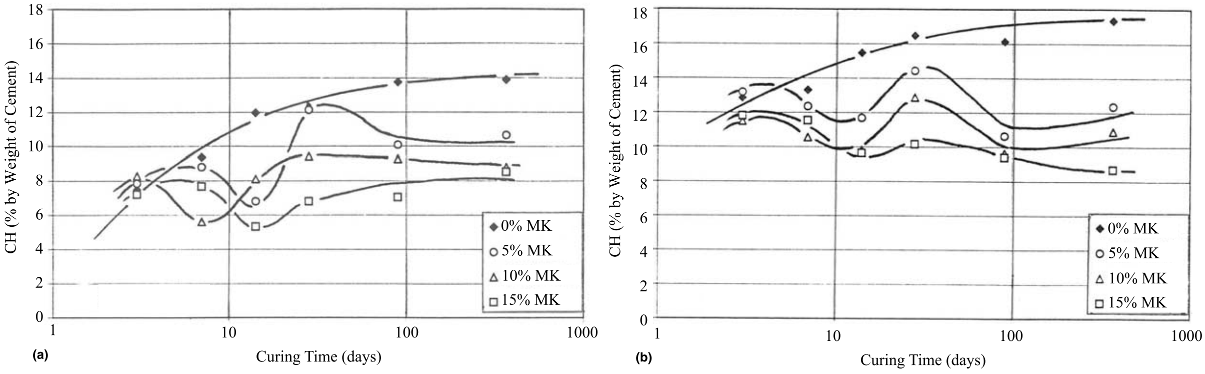

Fig. 2. Change in CH content vs curing time for MK: (a) mortar; (b) paste [38].

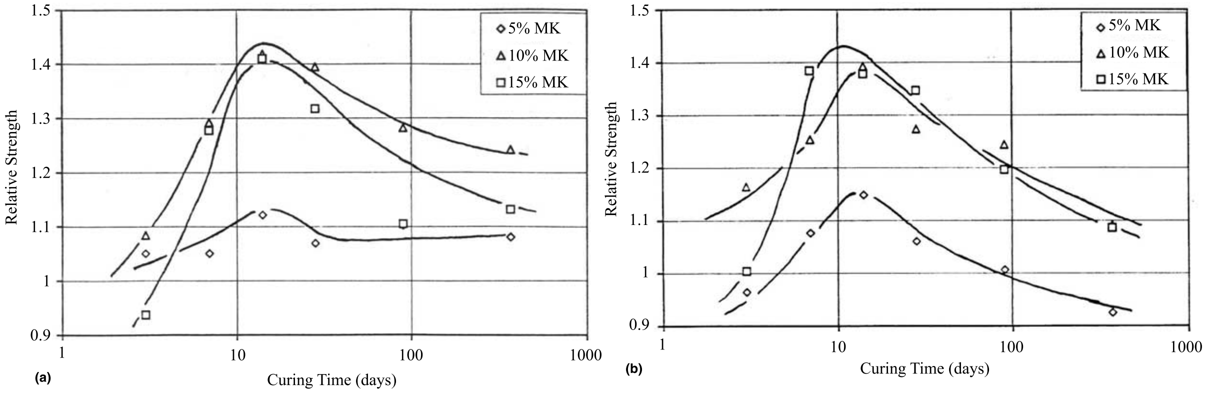

Fig. 3. Change in relative strength vs curing time for MK: (a) mortar; (b) paste [38].

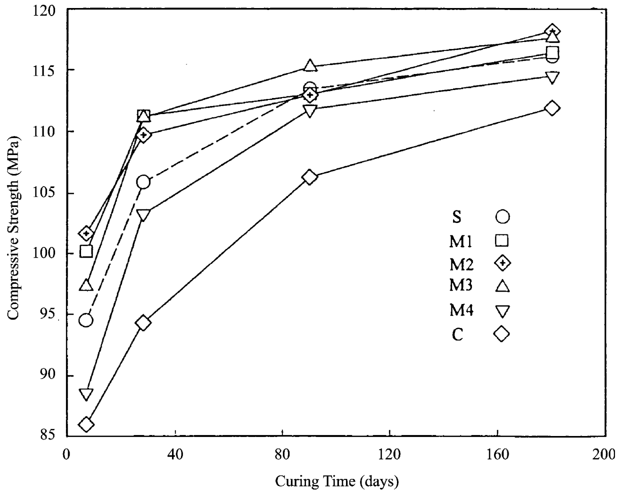

Fig. 4. Compressive strength vs curing time [40]. Mortar: C-control; S-silica fume; M1, M2, M3, M4 – MKs.

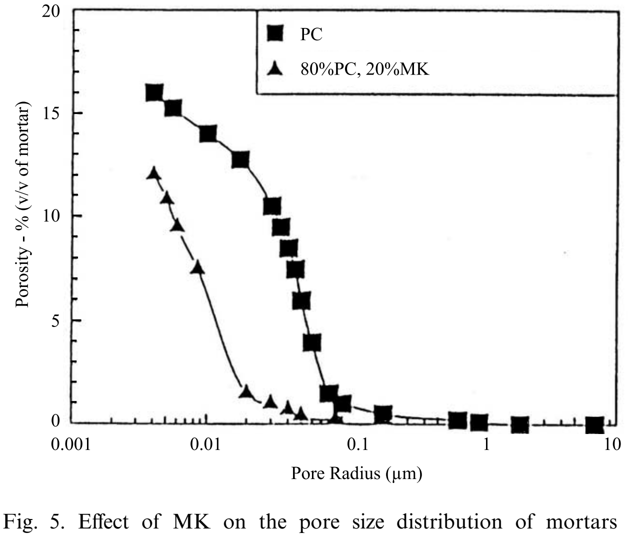

Fig. 5. Effect of MK on the pore size distribution of mortars – $w/b = 0.4$; aggregate/binder = 1.0; age = 100 days [29].

seen that significant reductions in the average pore size are obtained when the cement is replaced by 20% MK. It was also found [29] that MK is effective in reducing the rate of diffusion of Cl^- and Na^+ ions in mortar and also in reducing the rate of water absorption. In [41] it was reported that the pore structure of MK blended pastes is finer than that in plain cement paste. Hydrated blended cement with 30% replacement by MK contained mostly narrow necked pores (<0.03 μm) and the authors suggested that an improvement in durability under freezing and thawing conditions would be obtained. The pore structure of cement pastes, containing up to 15% MK, were also examined in [42], using mercury intrusion. It was found that the proportion of pores of radii < 0.02 μm within the pastes increased with increase in both MK content and curing time. The rate of pore refinement was very rapid up to 14 days curing after which pore size changed very little. This supports the observation made in the previous section that, though pozzolanic activity continues beyond 28 days, a significant proportion of the reaction occurs within the first 14 days when maximum relative strength is also achieved. However, although the total pore volume was found to decrease with increase in curing time it was found to increase with increase in MK content. Similar influences by MK on pore structure and diffusion rates of MK–PC pastes were reported by Cabrera et al. [31,43].

6. Chemical shrinkage and autogenous shrinkage

Wild et al. [22] studied the chemical and autogenous shrinkage and swelling of MK–PC pastes for MK contents in the range 5–25%. The specimens were monitored for periods between 1 and 45 days. At all times autogenous shrinkage was found to increase with increase in MK content up to a maximum at 10% MK, and then decrease for higher MK contents. This maximum was attributed to an optimum in the combined effect of cement hydration and pozzolanic reaction in removing water from the system at this composition. Chemical shrinkage was also found to reach a maximum between 10% and 15% MK and then decrease sharply for higher MK contents. Also pastes stored in water showed substantial expansion for MK contents above 10%. The reduced autogenous shrinkage, reduced chemical shrinkage and the substantial expansion in water for the pastes with high MK contents, relative to those with low MK contents, was attributed, in part, to the formation of increased amounts of C_2ASH_8 and reduced amounts of C_4AH_{13} as the MK content increased. This was thought to result in a relative increase in the volume of reaction products.

Rols et al. [44] measured autogenous shrinkage in concrete up to 24 h. They reported results for cementitious systems containing approximately 9% MK. At all times the autogenous shrinkage was found to be lower than that in the control specimens.

7. Compressive strength development

There have been several studies on the strength development of concrete containing MK. These studies have demonstrated clearly that with intelligent use considerable enhancement in strength, particularly at the early stages of curing, can be produced. Caldarone et al. [45] produced concretes, with 5% and 10% MK, which showed enhanced strengths at ages up to 365 days. They reported that their MK–PC concretes exhibited strengths, which were slightly greater than SF–PC mixtures at the same levels of cement replacement by the pozzolans. Similar influences of MK on the strength of concrete have been reported by Wild et al. [46]. The authors identify three elementary factors, which influence the contribution that MK makes to concrete strength. These are the filler effect, which is immediate, the acceleration of PC hydration, which occurs within the first 24 h, and the pozzolanic reaction, which has its maximum effect within the first 7–14 days for all MK levels between 5% and 30% [46]. The degree to which strength is enhanced declines beyond 14 days, although strength gains relative to the control are still present after 90 days. Also little strength advantage is gained for MK levels in excess of 15%. Similar findings were observed in [40] where strength gains in mortars containing 15% MK continued after 180 days.

The influence of curing temperature on the strength development in concretes containing up to 15% MK was studied by Sabir [47]. It was shown that curing MK concrete at 50°C results in increased early strength (7 days) compared to the strength of specimens cured at 20°C. The acceleration in strength development due to the high curing temperature diminishes in the long-term (365 days). In terms of the strength relative to that of the control concrete cured at 20°C, the optimum level of MK replacement for cement in concrete with $w/b = 0.35$ cured at 20°C was found to be about 10%. This level of MK was found to be reduced to about 5% for concretes cured at higher temperature (50°C) and with higher w/b ratio (0.45).

A recent study [48] has shown that as with SF and FA, MK has the effect of retarding the setting time of high strength concrete. In general, as replacement levels of the pozzolans were increased, there was greater retardation in setting times. However, for the concrete containing MK, this was only observed up to a replacement level of 10%.

8. Effects of MK on durability properties

As pointed out in Section 5, there is strong evidence that MK greatly influences the pore structure in pastes and mortars and produces substantial pore refinement. This leads to significant modifications to the water transport properties and diffusion rates of harmful ions. It has been reported [49] that MK reduces the volume of capillary pores of sizes (0.05–10 μm) normally associated with increased permeability. According to [49] the rate of water absorption of mortar is halved by replacing 20% of the cement by MK. The refinement of the pore structure effected by the MK was also found to reduce the rate of ingress of chloride ions into the concrete. Significant reductions in the values of the diffusion coefficient were obtained when 15% of the cement was replaced by MK. In addition Coleman and Page [50] have shown that cement pastes blended with 10% or 20% MK exhibited higher capacities than plain PC pastes, to bind chloride ions introduced by contamination of the mix water, thus reducing the Cl^- concentration in the pore solution. The MK also produces a long-term reduction in pore solution hydroxide ion concentration. However, although there is a reduction in pore solution pH, the $[Cl^-]/[OH^-]$ ratios are similar to those in equivalent plain PC pastes, from which it is concluded that inclusion of up to 20% MK will have little effect on the risks of chloride induced corrosion of embedded steel.

8.1. Alkali silica reaction

Walters et al. [28,51] determined the effectiveness of MK in suppressing ASR in concrete using mixtures containing inert limestone aggregate and chert/flint reactive sand. ASR tests were conducted on 75 mm × 75 mm × 220 mm concrete prisms in accordance with Draft British Standard Specification 812, Part 123. The authors [28] showed that without MK the concrete specimens exhibited an expansion of 0.45% after 6–9 months. The expansion was reduced to less than 0.01% when the standard PC they employed was replaced by 10–15% MK. It was reported that the cracks and surface deterioration, which were present in the control specimens, were virtually eliminated when MK was used. In another paper, Kostuch et al. [29] showed that expansion in concrete due to ASR is completely eliminated by replacing the standard PC used by 15% MK. The expansive product in the MK free concrete was identified as a "high Ca^{2+} gel" containing low levels of Na^+ and K^+ and the amount formed was dependant on the amount of CH available relative to the amount of active silica present. The role of MK in reducing expansion is therefore in reducing the amount of freely available CH and the CH/SiO_2 (active) ratio and hence preventing formation of a swelling gel.

8.2. Resistance to aggressive solutions

Marwan et al. [35] calcined lateritic soil at 800°C and employed it as blend admixture for concrete. At these temperatures the kaolinite present in the laterite converts to MK which is found to enhance performance under the attack of sea water and acidic solutions. Compositions with 20–50% calcined laterites were employed and the authors found that best performance was obtained when the cement is partially replaced by 30% calcined laterites which results in total elimination of CH produced in the cement hydration.

Bosc et al. [52] examined the durability of MK blended mortars when subjected to the action of sea water. Their specimens (20 mm × 20 mm × 160 mm prisms) were subjected to sea water after being air cured at 98% R.H. for 28 days. Curing and exposure temperatures of 20°C and 30°C were employed. At both temperatures best performance, as measured by compressive strength and expansion, was obtained in the case of mortars containing MK and a melamine superplasticiser. The MK mortars resulted in 40% increase in strength and 60% reduction in dimensional change relative to the control mortars. Cabrera and Nwaubani [43] examined MK–PC pastes exposed to sodium chloride in a standard diffusion cell and found that the diffusion rates of chloride ions were reduced below those of control mixtures.

The expansion of MK mortar bars due the action of sulphates was measured by Khatib and Wild [53]. The mortar specimens were immersed in a 5% Na_2SO_4 solution for periods of up to 520 days. Two types of cement, one with high and one with intermediate C_3A contents were used for a range of replacements by MK up to 25%. All tests showed remarkable reductions in expansion effected by the incorporation of MK. The reductions were increased as the MK content increased with complete suppression of expansion produced (after 520 days) using 20% and 25% MK. However, mortar containing MK levels of up to 10% exhibited a loss in strength in Na_2SO_4 solution, relative to equivalent water-cured bars, whereas bars containing MK levels in excess of 15% showed a gain in strength. Reduction in CH content was considered to be the primary factor by which MK improves sulphate resistance. The authors proposed that at least 15% replacement of cement with MK was necessary to provide good sulphate resistance.

In a recent paper, Martin [54] showed that MK could be used to improve the durability of concrete under the aggressive action of organic acids from silage effluents. Reduction of 30% in mass loss of concrete exposed to silage effluent was obtained by partially replacing cement with 15% MK. Pera et al. [55] examined the influence of MK on the resistance of concrete to solutions of lactic acid and ammonium sulphate simulating an aggressive agricultural environment. The results of this investigation showed that the presence of 10% MK limited the damage caused by exposure to lactic acid. It was also observed that while MK was found to be more pozzolanic than SF it was less effective in the more aggressive ammonium sulphate solution.

8.3. Other applications

Studies have also been conducted on the utilisation of MK in the immobilisation of hazardous wastes and toxic metals which have traditionally been done using a cement-based matrix. Pera and Bonnin [56] examined the performance of MK blended cement systems in the inertisation of heavy metals by adding toxic solutions of chromium, lead and cadmium into the mixing water of pastes and mortars. Based on measurements of strength and leaching properties they concluded that blends with 20% MK were effective in immobilisation of toxic metals. In another paper, Pera et al. [57] found that MK is effective in enhancing the retention of chlorides and sulphates present in municipal incinerator FA when the latter is used as a partial replacement for the sand in mortar.

In addressing durability problems related to concrete pavement, Barger et al. [58] developed a blended cement system containing calcined clay as a pozzolan. In addition to reduced susceptibility to ASR and improved resistance to sulphate attack, the calcined clay modified system resulted in lower heat of hydration and increased strength.

Girodet et al. [59] examined the freeze-thaw resistance of mortar specimens containing MK as a partial PC replacement under three point loading. As with SF, MK was found to improve the durability of the mortars tested. This was attributed to the pore refinement produced by the pozzolanic activity.

9. Influence of MK on workability

Although it is generally acknowledged that MK adversely affects the workability of concrete, no detailed examinations have been reported to-date on the water demand of MK and its influence on the flow properties of concrete. Caldarone et al. [45] observed that although the slump of concrete containing 10% MK was reduced from that of concrete with PC only, the MK concrete required 25–35% less high range water reducers (HRWR) than equivalent SF mixtures. This reduction in HRWR demand resulted in the MK concrete having less sticky consistency and better finish than the SF concrete. The initial time of set, for a 10% replacement for cement, although less than the control concrete, was found to be the same for both MK and SF concretes. Wild et al. [46] found it necessary to employ up to 3% superplasticiser to produce moderate slumps (75 mm) in MK concrete with w/b ratio of 0.45. Sabir et al. [60] reported that although it was clear that MK increased water demand, the standard workability tests, i.e., slump, compacting factor and Vebe time, were not capable of quantifying the influence on the overall flow properties of MK concrete, particularly at the lower w/b ratios ($w/b = 0.35$). Mixtures with low w/b ratios, although they appeared relatively dry, exhibited the good cohesion previously reported in [45] and compacted well on vibration. A more suitable test for MK mixtures may be the two-point test [61] used by Faroug et al. [62]. This test is based on the Bingham flow model, which gives parametric values that can be related to yield value and plastic viscosity as discussed earlier. In another paper Sabir [47] conducted a series of tests on concretes containing a range of MK substitutions for cement and for different w/b ratios and emphasised the need for HRWR. Rols et al. [44] also reported that the utilisation of MK requires higher quantities of superplasticiser compared to that in the control concrete. Bai et al. [63] reported a systematic decrease in both slump and compacting factor and a systematic increase in Vebe time as the PC replacement level by MK in their concrete mixtures increased from 0% to 15%. The authors [63] used two w/b ratios (0.4 with superplasticiser and 0.5 without) and observed that larger changes in workability occurred for the concretes with the high w/b ratios. Lota et al. [64] found that using a combination of MK and a polymer admixture, where the MK is used as an additive rather than a partial cement replacement, resulted in substantial workability improvement over that of the control mortar.

10. Comparison between metakaolin and other pozzolans

Typical oxide analyses of various pozzolans, GGBS and PC are shown in Table 2. It is seen that although the acidic oxides (silica and alumina) contents vary widely from one pozzolan to another, the common feature of natural and processed pozzolans is that silica is a major component of their composition. The glassy silica in natural pozzolans is formed by rapid cooling of molten lava, which normally consists of porous spherical particles. The glassy amorphous structure of artificial waste product pozzolans (e.g., FA and SF) and GGBS is also formed by rapid cooling. In the case of MK the crystalline structure is broken down by calcination at temperatures, which are in general lower than those necessary to generate liquid phase and produce glass on cooling.

The pozzolanic reactivity of calcined clays is associated with the removal of the structural water from the crystalline clay layers producing an amorphous or semi-amorphous product of high surface area and high chemical reactivity [7]. The necessary calcining temperature depends upon the nature of the clay mineral and the thermal energy required to release the hydroxyl ions. Grinding may also be advantageous in breaking up particle agglomerates and exposing additional surface for reaction.

Table 2
Chemical compositions of PC, GGBS and various pozzolans

Pozzolan	Mass percentage							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	$Na_2O + K_2O$	SO_3	LOI
PC [63]	21.0	4.63	2.26	65.6	1.18	0.94	–	0.99
GGBS [30]	34.0	16.0	0.32	36.92	8.83	0.87	2.67	0.0
FA [63]	49.1	26.4	9.3	1.4	1.4	5.0	0.8	4.9
SF [73]	92.0	0.7	1.2	0.2	0.2	2.0	–	3.0
MK [63]	52.1	41.0	4.32	0.07	0.19	0.89	–	0.6
Ground clay brick [10]	54.83	19.05	6.0	9.39	1.77	3.65	2.9	1.48

Although there are several theories underlying the reactivity of pozzolans, it is universally accepted that the principal cementitious reaction is facilitated by the dissolution of the glassy/amorphous silica, producing silica in solution in the pore water, which then reacts with the CH to form CSH gel. Alumina will also dissolve in the high pH environment. A small amount is incorporated in the C–S–H gel but the bulk reacts to form (normally crystalline) CAH and CASH phases, which may also assist in the cementation process and contribute to strength. The dissolution rate will depend on the specific surface, which is the main factor behind the different activities shown by the various pozzolanas with respect to the time taken to produce strength enhancement in concrete. In the case of concrete incorporating FA as partial cement replacement, for example, the strength is initially less than that of the control. This is due to the reduction in cement content and the slow rate of dissolution of silica effected by the relatively small specific surface of FA (typically 300–400 m^2/kg). With time, however, more of the silica goes into solution, and thus on reaction, forms additional CSH gel which leads to strength enhancement in the longer term. The SF and MK particles are, on the other hand, very finely graded with specific surfaces of order 50 times that of FA. This explains the rapid enhancement in strength when SF or MK are incorporated in concrete. The high surface area of MK increases water demand and, therefore, for a given w/b ratio and cement content, it reduces workability although not apparently as critically as for SF concrete. In contrast, FA is found to improve the flow properties of concrete. This is in part because of the spherical nature of its particles and also because of the adherence of the small fraction of very fine FA particles onto the cement grains which results in greater dispersal.

In general, it is found that the use of pozzolans as partial cement replacement materials for PC in concrete results in more densified concrete with reductions in diffusion rates of gases and ions and subsequently improved durability. Also ultra-fine FA, SF and MK rapidly remove much of the chemically active and 'harmful' CH from the concrete. The contrasting behaviours of various pozzolanas with respect to strength development and workability and also their relative costs have led some investigators to examine ternary blends containing MK with a view to utilising the beneficial properties of the different pozzolans.

11. Ternary blends containing MK

Asbridge et al. [30] examined concretes employing blends of PC/GGBS/MK with the intention of combining the environmental, low cost and high strength benefits derived from GGBS and the reduction in porosity and removal of CH caused by MK. Such utilisation should result in economic concrete with exceptional durability in aggressive environments. Concretes with weight ratios of PC/GGBS of 70/30, 50/50 and 30/70 were examined. In these mixtures MK was used at different levels, as a partial substitution for the PC-GGBS blend. It was stated that whilst no adverse effects on compressive strength were caused by the MK, the strengths at 96 days were significantly increased. Mercury intrusion porosimetry studies on portions of mortar, Fig. 6, showed that, whilst GGBS decreased the total pore volume, further reductions were effected by the MK. In contrast to slag, which produced an increase in the proportion of the large (>0.1 μm radius) pores, MK decreased this proportion and produced a more refined pore structure. Because of the improvement in the pore structure, removal of CH and reduction in diffusion rates, the authors [30] concluded that the ternary blends they examined would produce more durable concrete.

Caldarone and Gruber [65] examined ternary blends for concrete containing FA and MK or GGBS and MK. They found that in both ternary systems the compressive strength was improved when MK was added. The chloride permeability was also found to decrease relative to that when MK was not added.

In a recent study, Sabir et al. [66] examined the compressive strength of concrete made with PC/FA/MK blends. Fig. 7 gives the variation in relative strength, defined as the ratio of the compressive strength of the MK concrete to the strength of the control at the same age, with curing time. It was found that significant loss in early strength (up to 28 days) as a result of the incorporation of FA, particularly with the higher FA levels (20–30%), was restored by the incorporation of MK in the blend. This was attributed to the pozzolanic reaction of MK with the CH, which produced 40% enhancement in the 14 day strength, over that of the control, when 20% of the cement was replaced by MK. It was noted that even with such levels of MK, the long-term strength was not adversely affected.

Bai et al. [63] carried out a detailed study on the workability of concrete incorporating FA and MK as partial PC replacements with and without superplasticiser. Fig. 8 shows the iso-slump maps obtained in [63] for w/b ratios of 0.4 and 0.5. The contrasting effects on workability brought about by FA and MK made it is possible to design mixtures with various blend compositions for a given slump. In another paper [67], Bai et al. demonstrated the contrasting effects of FA and MK on the strength development in concrete. The reduction in early strength due to FA can be compensated by the inclusion of MK. Early strengths surpassing that of the control can be obtained with low partial cement

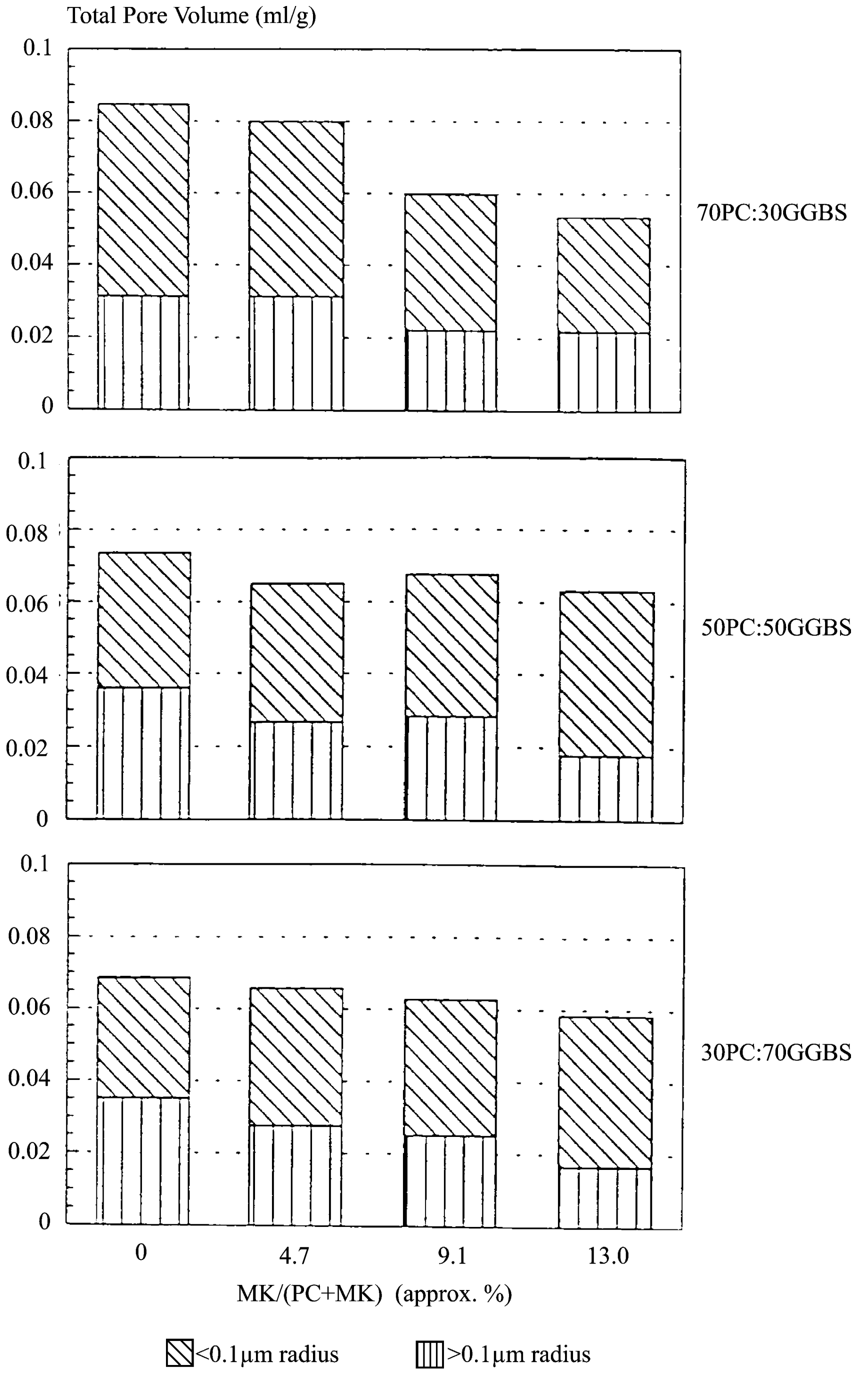

Fig. 6. Porosimetry data for PC-GGBS blends incorporating MK [30].

replacements and high MK/FA ratios. Higher cement replacements (40%) with low MK/FA ratios resulted in 90-day strengths that are greater than the strength of the control. It was further shown [67] that with careful choice of compositions it is possible to reduce the PC contents without reductions in compressive strength. Concretes incorporating PC–FA–MK blends are expected to exhibit superior performance with regards to durability. Several durability aspects are currently being studied by the authors and early indications appear to vindicate such expectations. Their findings [63,67] demonstrate that with intelligent use, the contrasting behaviours can be utilised with maximum benefit in terms of the finished product with respect to the flow behaviour, strength development and cost.

The chemical shrinkage in PC–MK–FA blended pastes was examined by Kinuthia et al. [68]. They reported that shrinkage is significantly increased by PC

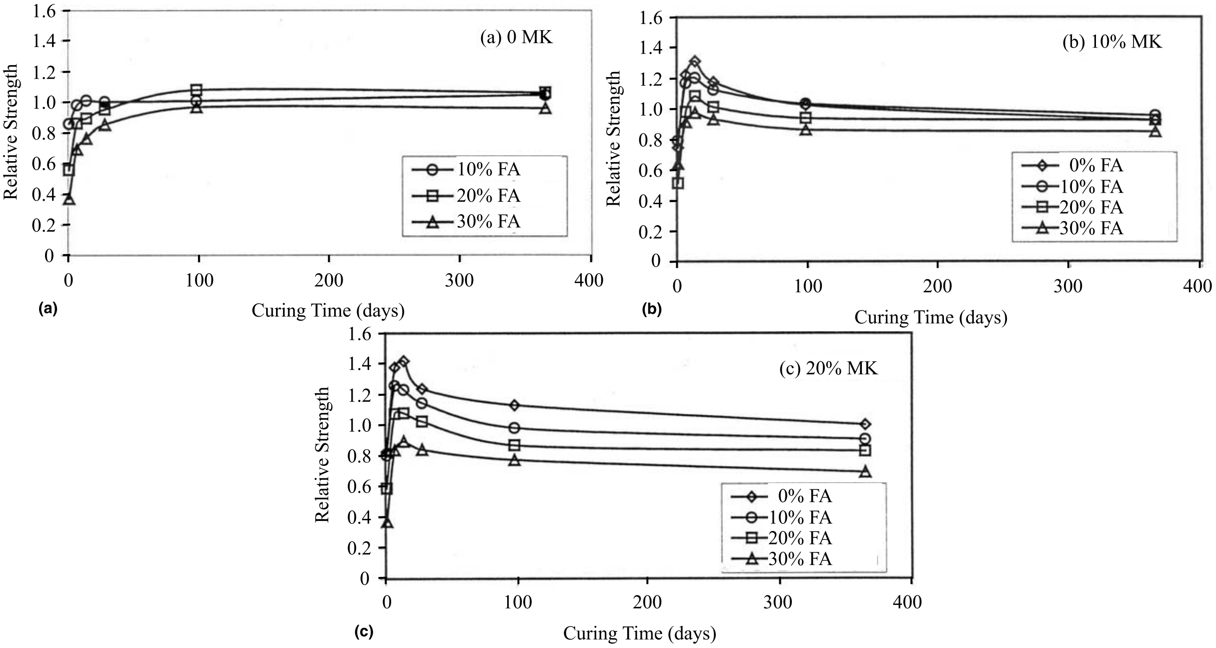

Fig. 7. Relative strength of FA–MK blended concrete [66].

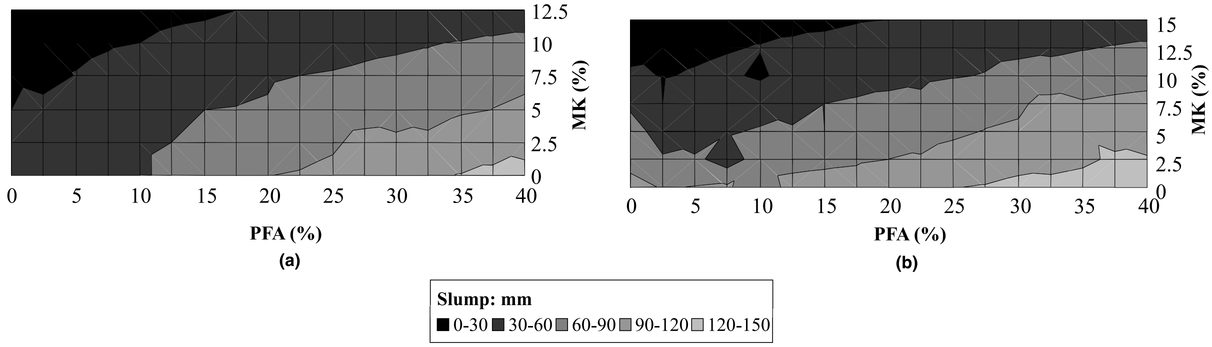

Fig. 8. Iso-slump maps for PC–PFA–MK blended concretes with: (a) $w/b = 0.4$; (b) $w/b = 0.5$ [63].

replacement of 10% FA or 10% MK and FA. In a paper by Wild et al. [22] where autogenous shrinkage was examined it was reported that MK has expansive effects in contrast to the shrinkage effects of FA. In PC pastes blended with MK and FA these influences combine in a complex and approximately compensating manner. Such observations should make it possible to design blends which show negligible shrinkage or expansion thus controlling or eliminating cracking.

12. Sources for metakaolin

As discussed in the previous sections MK is normally produced by calcining pure clays at appropriate temperatures. Ambroise et al. [27] demonstrated that MK can also be obtained by the calcination of indigenous lateritic soils. On calcination of laterites in the range 750–800°C, kaolinite and gibbsite are transformed into transition phases of MK and amorphous alumina both of which possess pozzolanic properties. Pera and Ambroise [69] showed that blended cements containing 30% calcined laterites produced strengths (between 7 and 28 days) higher than that of plain PC pastes. At 180 days the strength of paste containing 50% calcined laterites was 87% of that developed by plain PC.

Another source for the production of MK is that of calcining waste sludge from the paper recycling industry. Pera and Ambroise [70,71] showed that calcination of waste paper sludge at about 700°C produces highly reactive MK. Using DTA to evaluate the CH consumption in PC pastes blended with calcined sludge, the authors [70] found it insufficient to explain the pozzolanic activity on the basis of the kaolinite content of the calcined sludge. It was shown, by multiple linear regression analysis, that the main parameters influencing the pozzolanic activity were the quantities of kaolinite in the inorganic fraction, CH derived from the calcite present in the sludge and particle sizes smaller than 10 μm. Pera and Amrouz [72] found that despite a smaller kaolinite content, the DTA analysis showed that burnt paper sludge exhibited more pozzolanic activity than commercially available MK, particularly at early ages. This was attributed to the presence of superficial defects that occur during the calcination of the sludge.

13. Concluding remarks

It may be argued that the most important development in concrete production in the last century is the utilisation of industrial by-products such as FA and ground granulated blast-furnace slag as partial cement replacement materials [73]. This utilisation is now extended to other by-products including, SF and other pozzolanic wastes, e.g., rice husk ash. The volume of pozzolanic by-products produced world-wide currently exceeds that utilised. Many of these by-products contain toxic elements which can be hazardous if they find their way into ground water when dumped or disposed of as land fill or used for road-bases [74]. Increase in the utilisation of pozzolanic materials in concrete will come from greater awareness of current and potential uses of alternative and recycled materials and wider realisation of the environmental benefits accrued. Such increase in use of waste materials will contribute to the requirements of environmental protection and sustainable construction in the future. It has also been reported [73] that the supply of suitable FA and slag for blending with cements is, in some countries, becoming more and more limited. There are compelling reasons therefore, to extend the practice of partially replacing cement in concrete and mortar with waste and other less energy intensive processed materials, which have pozzolanic properties. One possible source for the production of such a pozzolan, i.e., MK, is natural clay.

The use of MK as a partial cement replacement material in mortar and concrete has been studied widely in recent years. The work reviewed demonstrates clearly that MK is a very effective pozzolan and results in enhanced early strength with no detriment to, and some improvement in, the long-term strength. MK alters the pore structure in cement paste, mortar and concrete and greatly improves the resistance to the transportation of water and diffusion of harmful ions which lead to degradation of the matrix. Presently MK is more expensive than PC, as is SF, even though its processing involves moderately low temperatures and its overall production cost is significantly less than that of PC. Wider realisation of the benefits of MK in mortar and concrete will lead to greater demands and this will inevitably drive costs down.

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